

MODELING UREA TRANSPORT AND AMMONIA VOLATILIZATION 54

UNDER FIELD CONDITIONS

by

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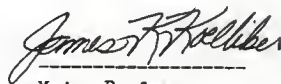
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INTRODUCTION

The synthesis of urea by Wohler, in 1828, was a landmark in the history of civilization. It was the first time that a substance produced by living beings had been prepared in the laboratory, thus opening up a new frontier in the field of chemistry. This new field of synthetic organic chemistry has undergone a tremendous expansion since its inception in 1828, and has made available to mankind, many useful products of which urea is one. In contrast to its laboratory preparation from ammonium cyanate in 1828, urea is commercially synthesized from hydrogen, nitrogen and carbon dioxide, with liquid ammonia as an intermediate product. The annual production of urea in the United States is in excess of 3.5 million tons and its principal use is as a high nitrogen content (46%) solid fertilizer.

Urea may be applied to soils either on the surface (unincorporated), or below the soil surface (incorporated). There is an increasing trend in the farming practice, in the United States, toward unincorporated application of fertilizer. This trend may be attributed to the fact that fertilizer placement below the soil surface is labor-intensive and time-consuming. At the same time, the practice of conservation tillage and reduced tillage has given a boost to surface application of fertilizer. Hendrickson et al. (1987) point out that surface application of urea to reduced tillage soils leads to rapid hydrolysis of urea owing to the high activity of the urease enzyme in the presence of surface residue. It follows from the chemistry of

soils that high hydrolysis rates of urea lead to a high concentration of ammonium ions which is responsible for the high loss of urea-nitrogen in the form of ammonia volatilized.

Despite the awareness of the fact that surface applications of ammoniacal nitrogen result in relatively higher ammonia-N losses as demonstrated by Fenn and Kissel (1976), the practice of unincorporated application of urea is likely to continue. Thus, the current trends in farming practice dictate the need to develop a better understanding of the many factors and processes that influence ammonia volatilization. From an environmental viewpoint, a better understanding of solute transport processes in the unsaturated zone of the subsurface is necessary. This is so because in modern agricultural practice, application of hazardous chemicals such as pesticides and herbicides has led to the contamination of soil and the pollution of groundwater. It is therefore, important to investigate the processes that control the transport of these chemicals from the soil surface to the groundwater table. Another environmental consideration is that volatilization of ammonia leads to significant air pollution, especially in farmlands. Hence, the need exists to quantify the magnitude of this loss. Further, fertility management considerations underline the need to obtain more reliable quantification of interchanges of nitrogen in the soil-water system.

The factors that influence volatilization loss of ammonia from urea fertilizer may be grouped into three categories, namely, soil properties, environmental conditions and fertilizer management. The properties of soil that are of relative importance are texture, pH,

cation-exchange capacity, hydrogen-ion buffering capacity, calcium carbonate content, respiration rate, urease activity, temperature and water content. The environmental conditions that influence ammonia loss are air temperature, solar radiation, relative humidity, wind speed, amount of precipitation and timing of precipitation. The significant factors in fertilizer management are application rate, depth and method of fertilizer placement and irrigation pattern.

All of these factors interact in a way that allows heat, mass and momentum transfer to occur simultaneously at and below the soil surface. Owing to the complexity of this system, it is difficult to simulate, in the laboratory, field conditions responsible for ammonia volatilization loss. The literature provides many useful laboratory techniques to simulate field volatilization losses. One laboratory technique proposed by Bouwmeester et al. (1985) involves the use of a wind tunnel in contrast to earlier models that utilized static enclosures or flow-through systems with constant air movement. But, no matter how sophisticated a laboratory technique may be, it is merely a representation of reality and such representation may or may not be close to reality. Therefore, results obtained from laboratory techniques or computer models, should not be evaluated in absolute terms, but rather, in relative terms.

Owing partly to differences in the methods used in laboratory and field measurement of ammonia volatilization, there is much discrepancy in the ammonia loss values reported in the literature. For example, Hargrove et al. (1987) measured different amounts of ammonia volatilization loss for a forced-draft technique in comparison to a Nitrogen-15

recovery technique under identical field conditions. Titko et al. (1987) point out that one study reported a loss of 39% urea-N applied to thatchy turf while another study found a loss of only 1.6% from the application of prilled urea to turf. Inconsistencies, such as the one cited by Titko et al. (1987), may be misleading, especially, if a volatilization loss figure is quoted without mention of the major factors that are responsible for the loss.

Generally, field studies on ammonia volatilization are expected to provide more reliable results if satisfactory measurement techniques are used. However field studies are time-consuming, cumbersome and expensive. Hence many researchers tend toward laboratory measurement or computer modeling. While computer modeling is not a substitute for field studies, it is, nevertheless, a powerful tool. The availability of reliable data is necessary for computer simulation. However, an attempt to model a system with inadequate data can also be instructive as it may serve to identify those areas where detailed data are critical to the success of the model.

With these perspectives in mind, a computer model, that simulates ammonia volatilization under field conditions, was developed further and is presented as the research for this thesis. The model is used to predict ammonia volatilization losses over a 15-day period following application of urea to Haynie soil. The model utilizes the 15-day meteorological data-set collected by McInnes (1985) during field measurement studies on ammonia volatilization. The results predicted by the model are compared with field results reported by McInnes et al. (1986).

A computer model, for ammonia volatilization, in which constant soil temperature and constant soil moisture are assumed, was developed in the Department of Agronomy at Kansas State University. This model is described in the Annual Report (1985) to Farmland Industries. The utility of this model is limited because under field conditions, soil moisture and temperature undergo dramatic changes with concomitant changes in the rate of urea hydrolysis and ammonia volatilization. The effect of soil moisture and soil temperature on the urea hydrolysis rate is well-documented in the literature. Bremner and Mulvaney (1978) provide an excellent literature survey of the effect on urease activity as affected by soil water content and temperature. In recognition of this fact, an attempt was made as described in the Annual Report (1985) to combine the constant temperature and moisture model with a model developed by McInnes (1985) for predicting diurnal variations in soil temperature and soil moisture. The model thus obtained was referred to as the Combined Model in the Annual Report (1985). The Combined Model was flawed in that it predicted negative urea hydrolysis.

The research presented in this thesis was initiated with the short-term objective of correcting the problem of negative urea hydrolysis in the Combined Model. The Combined Model was developed on a PDP-11 minicomputer system in the Evapotranspiration Laboratory at Kansas State University. Since access to the PDP-11 computer system was limited, it was decided to adapt the model to a Personal Computer equipped with a numeric coprocessor to enhance the computation speed.

The work presented in this research is divided into four stages. In the first stage, changes were made in the programming code of the

Combined Model so as to adapt it to the syntax of Microsoft FORTRAN and hence to develop a Personal Computer-based model (PC Model). The second stage of this research involved the recognition and correction of the problem that led to the prediction of negative urea hydrolysis. Additionally, in the second stage, the PC Model was tested with a 4-day test data set. The results obtained from the test runs led to the incorporation of soil respiration in the model. At the same time, two subroutines were added to the model in order to verify mass balances for ammoniacal and carbonate species as well as the mass balances for calcium ions and hydrogen ions. Also, some existing equations in the model were modified and corrected. In the third stage, the 15-day meteorological data set collected by McInnes (1985) was modified to permit its utilization in the model. Preliminary results obtained from test-runs of the model with the 15-day data set suggested the need to include convective mass transfer for all chemical species. Hence, a further accomplishment for the third stage of this research was the addition of a subroutine to compute convective transport of solute and to include its effects on the mass balances for all chemical species. Finally, in the last stage, the model was used to compare predicted results with field results and was also used to test its sensitivity to various parameters.

The thesis has been divided into three chapters. In Chapter 1, the theory of ammonia volatilization from surface application of urea to soils is presented. Chapter 2 describes and discusses the development of the PC Model. In Chapter 3, results predicted by the model are interpreted and compared with field results. Further, results for sensitivity analysis of the model are presented and interpreted. Finally, in Chapter 3, conclusions from this research and recommendations for future work to improve the model are given.

Chapter 3 of this thesis is followed by three appendices. Appendix A contains a listing of the PC Model. Appendix B contains documentation for the model. Appendix C gives all tabulated data used in the thesis.

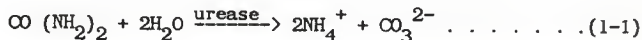
CHAPTER 1

THEORY OF AMMONIA VOLATILIZATION

In this chapter, theoretical considerations for modeling ammonia volatilization will be discussed. The various factors that affect ammonia volatilization were listed in the Introduction to the thesis. In general, urea hydrolysis rate, equilibrium chemistry of soils and the processes of heat, mass and momentum transfer, all have a pronounced effect on ammonia volatilization. Modeling ammonia volatilization therefore necessitates a fundamental understanding of the general criteria given above. It should be noted that the term mass transfer includes solute transport, both in the aqueous and gaseous phases.

Urea Hydrolysis

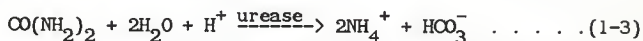
Urea $[\text{CO}(\text{NH}_2)_2]$ hydrolyzes in the heterogeneous system consisting of soil, soil air soil water (to be referred to as soil for simplicity) according to the following irreversible, enzyme-catalyzed reaction:



At soil pH less than 8.3, the carbonate ions (CO_3^{2-}) formed are almost entirely converted to bicarbonate ions (HCO_3^-) according to the following reaction:



Urea hydrolysis is frequently represented by the net reaction which is obtained by adding equations (1-1) and (1-2) and is given by:



Equation (1-3) suggests that for each mole of urea hydrolyzed, one mole of hydrogen ions (H^+) are removed from soil. In fact, at soil pH less than 8.3, HCO_3^- formed may react with H^+ to form carbonic acid (H_2CO_3), the extent of the reaction depending on soil pH. This reaction, along with other reactions that comprise the carbonate system equilibria will be discussed in detail later in this chapter.

The net effect of urea hydrolysis is to raise the soil pH. The activity of the enzyme, urease, is affected by soil pH, soil temperature, soil moisture, soil organic carbon content and urea concentration. It is beyond the scope of this research to investigate, in detail, the kinetics of urea hydrolysis which is an area of research by itself. Therefore, only a brief discussion of the factors affecting urea hydrolysis is given.

Urease activity increases with an increase in soil pH up to a soil pH in the range 6.0 to 7.0. This statement follows from the experimental results of Petit et al. (1976) and Singh and Nye (1984). However, Tabatabai and Bremner (1972) and May and Douglas (1976) found the optimum pH for soil urease activity to be in the pH range 8.8 to 9.0. Based on the studies of Petit et al. (1976) and Singh and Nye (1984), it is assumed, in this research, that the optimum pH is 6.5.

Urease activity was found by Singh and Nye (1984) to increase with urea concentration until an optimum urea concentration was

reached. Increase in urea concentration beyond the optimum value decreased urease activity, owing to substrate inhibition. In the model presented in this research, the effect of concentration is incorporated in the model by using a Michaelis-Menten type of relation to describe urea hydrolysis rate. It is assumed that substrate inhibition does not occur.

The effect of temperature on urea hydrolysis rate is accounted for by the Arrhenius equation. The effect of organic carbon content of soil on $v_{\max}$ is estimated from the data of Zantua and Bremner (1977). Finally, the effect of soil moisture on urea hydrolysis rate was determined from the data of Vlek and Carter (1983) and from the data of Kissel and Cabrera (1988).

The final form of the equation used to describe urea hydrolysis rate is:

$$v = \frac{v_{\max} * C}{K_m + C} * PEFF * PHEFF \dots \dots \dots (1-4)$$

where:

v = urea hydrolysis rate, $\text{kmol}/(\text{kg soil})(\text{s})$

$v_{\max}$ = maximum urea hydrolysis rate which includes the effect of soil organic carbon content of soil and soil temperature, $\text{kmol}/(\text{kg soil})(\text{s})$

C = urea concentration, kmol/m^3 soil sol

K_m = Michaelis - Menten constant, kmol/m^3 soil sol

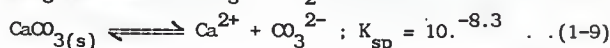
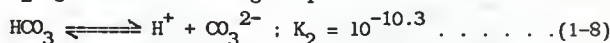
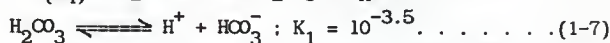
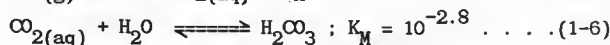
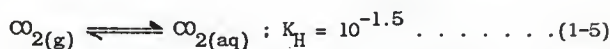
$PEFF$ = a factor to account for the effect of soil moisture, dimensionless

$PHEFF$ = a factor to account for the effect of soil pH, dimensionless

Carbonate System Equilibria

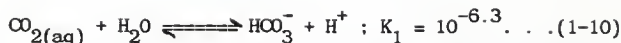
The pH of soil is further influenced by the equilibria of the carbonate system and the equilibria of the ammonia system which in turn are affected by the processes of heat, mass and momentum transfer. A fundamental understanding of the carbonate system equilibria is, therefore, necessary in order to account for its effect on soil pH.

The following reactions, primarily, govern the equilibria of the carbonate system:



The values for the equilibrium constants (K-values) were obtained from Snoeyink and Jenkins (1980) and are applicable at a temperature of 25°C. For the model presented in this research, the values for the equilibrium constants are expressed as functions of temperature. The functional relations were obtained from Hales and Drewes (1979).

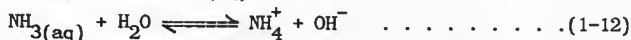
At 25°C, the ratio of the concentration of H_2CO_3 in solution to the concentration of aqueous carbon dioxide $[\text{CO}_{2(aq)}]$ is approximately 1.6% (Snoeyink and Jenkins, 1980). The ratio is small at other temperatures also, suggesting that for modeling purposes, equations (1-6) and (1-7) may be combined to eliminate H_2CO_3 from the carbonate system equilibria. Thus, the addition of equations (1-6) and (1-7) yields:



Functional relations for K_H , K_1 , K_2 , and K_{sp} completely describe the carbonate system equilibria.

Ammonia System Equilibria

The equilibria of the ammonia system is represented by the following equations:



The equilibrium relation represented by equation (1-12) is frequently written in an alternate way:



In the present research, the equilibrium given by equation (1-13) is assumed to be a cation-exchange reaction in which ammonium ions (NH_4^+) are adsorbed on the solid phase of soil. The adsorption of NH_4^+ releases calcium ions (Ca^{2+}) in the soil solution. Hence, equation (1-13) may be written in the alternate form:



The equilibrium constant for equation (1-15) is frequently given by a Gapon type of relation which is not used in this research.

Instead the equilibrium between NH_4^+ and $\text{NH}_4^+(\text{ad})$ is assumed to be represented by the Freundlich equation:

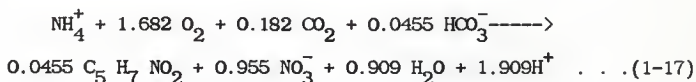
$$[\text{NH}_4^+(\text{ad})] = \text{NK}_1 [\text{NH}_4^+]^{\text{NK}_2} \dots (1-16)$$

The value of the Freundlich equation constant, NK_2 , was obtained from the data given by Singh and Nye (1986). The value of NK_1 was taken to be approximately five times the value given by Singh and Nye (1986).

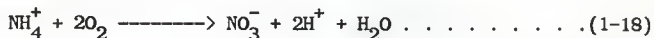
The equilibrium constants for equations (1-11) and (1-14), were obtained, as a function of temperature, from Hales and Drewes (1979). The temperature-dependent values of Henry's Law constant for the solubility of ammonia were modified in order that the computed values for the partial pressure of ammonia in soil air were in reasonable agreement with the corresponding measured values reported by Blanchard (1967). Similarly, the values of Henry's Law constant for carbon dioxide solubility in water were modified in view of experimental results obtained by Greenwood (1970). These results indicate a disequilibrium between carbon dioxide in the gaseous phase of soil and carbon dioxide in the aqueous phase owing to the slow diffusion of carbon dioxide in the aqueous phase. The results further show that the rate of change of the partial pressure of oxygen in soil air is at least 20 times the rate of change of partial pressure of carbon dioxide in soil air. This suggests that approximately 95% of carbon dioxide produced in soil as a result of respiration (oxygen consumption), remains in solution.

The ammonia system equilibria may also be influenced by the biochemical oxidation of ammonium ions to nitrate. This reaction is referred to in literature as nitrification which is mediated in soil by two aerobic, autotrophic micro-organisms, namely, *Nitrosomonas* and *Nitrobacter*. *Nitrosomonas* converts ammonium ion to nitrite while

Nitrobacter converts nitrite ion to nitrate. The overall reaction for nitrification proposed by McCarty et al. (1969) is:



A simpler form of nitrification reaction, which may be used in modeling work is:



Theoretically, nitrification tends to lower the soil pH. An inspection of equation (1-18) reveals that for each mole of ammonium ions oxidized, two moles of hydrogen ions are released. From a theoretical standpoint, nitrification appears to contribute significantly to lowering the pH. Practically, however, nitrification may be insignificant for the time period considered to model ammonia volatilization. In BOD measurement of wastewater, nitrification is taken to be insignificant for the 5-day BOD test. For the present research, it was assumed that the effect of nitrification on soil equilibria is negligible. This assumption was necessary because field data on nitrification were not available.

Effect of Soil Equilibria on Soil pH

An inspection of the various equations describing the carbonate system equilibria and the ammonia system equilibria reveals that soil pH is the master variable affecting soil equilibria. In fact, the key to modeling ammonia volatilization is to be able to accurately predict the soil pH, particularly at the soil surface. Based on the Lewis and

Whitman "two-film theory", also referred to as the "two-resistance theory" (Treybal, 1980; Hines and Maddox, 1985), ammonia loss due to volatilization is given by:

$$NH_3LOS = \frac{NH_3G(2) - NH_3G(1)}{RNH_3} \dots \dots \dots (1-19)$$

where:

NH_3LOS is the volatilization loss of ammonia, $kmol/(m^2)(s)$;

$NH_3G(2)$ is the concentration of ammonia in the soil air within the surface layer of soil, $kmol/(m^3 \text{ soil air})$;

$NH_3G(1)$ is the concentration of ammonia in the air above the soil surface, $kmol/(m^3 \text{ soil air})$;

RNH_3 is the resistance to mass transfer of ammonia from soil surface, s/m .

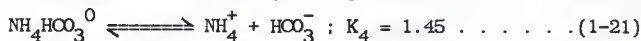
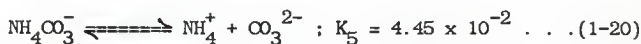
The term, $NH_3G(1)$, in equation (1-19), is relatively insignificant compared to $NH_3G(2)$ and is assigned a constant value. This implies that if RNH_3 is predicted accurately, ammonia loss can be quantified accurately provided an accurate prediction of $NH_3G(2)$ is possible. The last statement is an oversimplification of the task to model ammonia volatilization. Nevertheless, it points to the significance of two variables whose values dictate what the volatilization loss will be. In the present research, RNH_3 is set equal to the resistance to mass transfer of water vapor from the soil surface (RA). This is based upon Higbie's "penetration theory" (Treybal, 1980; Hines and Maddox, 1985) which states that for different solutes under the same circumstances, the mass transfer coefficient (reciprocal of resistance to mass transfer) is proportional to the square root of the diffusion coefficient of the solute. The diffusion coefficients for water vapor and ammonia, calculated from the equation proposed by Fuller et al.

(1966), are approximately equal. It follows that the mass transfer coefficients for water vapor and ammonia should be approximately equal. In the present research, the computation of RA is based upon the model developed by McInnes (1985) for prediction of diurnal variations in soil moisture and soil temperature. The predicted soil moisture and soil temperature results agree fairly well with field measurements, suggesting that the computation of RA is reasonably accurate. The foregoing considerations point out that $\text{NH}_3\text{G}(2)$ values will dictate the magnitude of ammonia loss. $\text{NH}_3\text{G}(2)$ values are obviously, dependent on the equilibria of the ammonia system. What is not so obvious is that $\text{NH}_3\text{G}(2)$ values are also indirectly dependent on the equilibria of the carbonate system. The last statement is based on the fact that the equilibria of the two systems affects soil pH which in turn influences the equilibria of the two systems.

Hence, it may be concluded that soil pH is a master variable and prediction of changes in soil pH is fundamental to modeling ammonia volatilization. The next sections of this chapter are, therefore, devoted to developing a qualitative understanding of, and deriving quantitative relations for, the effect on soil pH due to: urea hydrolysis, soil respiration, carbon dioxide loss from soil surface, ammonia volatilization, adsorption or desorption of ammonium ions and finally, precipitation or dissolution of calcium carbonate.

According to Marion and Dutt (1974), soil equilibria is affected by the formation of complex ions, particularly, ammonium carbonate complex ions, $(\text{NH}_4\text{CO}_3^-)$ and ammonium bicarbonate $(\text{NH}_4\text{HCO}_3^0)$. Thus in the

analysis of soil equilibria, the following reactions are additionally considered:



Since the dependence of K_4 and K_5 on temperature was not available, it is assumed that K_4 and K_5 are constant for all temperatures. This assumption may introduce an error in soil equilibria calculations. However, since the concentrations of the two ion pairs are relatively small, the use of constant values for K_4 and K_5 is not expected to introduce significant error. Further, in quantifying the effect of soil pH due to the several reactions that disturb soil equilibria, the equilibria represented by equations (1-20) and (1-21) is ignored. Once again, owing to the negligibly small concentrations of the two ion pairs, it is assumed that the omission of equations (1-20) and (1-21) from the analysis for soil pH will not introduce a significant error. A qualitative discussion of the effect on soil pH due to the several reactions that disturb soil equilibria follows. A graphical illustration of the effect on soil pH is given in Figure 1-1.

As mentioned earlier, urea hydrolysis raises the pH of soil. This is best understood by examining equation (1-1) which represents the hydrolysis of urea. The products of urea hydrolysis are NH_4^+ and CO_3^{2-} . The production of NH_4^+ disturbs the equilibrium between NH_4^+ and aqueous ammonia $[\text{NH}_3(\text{aq})]$. The equilibrium between the two chemical species is given by equation (1-14). For a given temperature, the equilibrium constant (K_2) for equation (1-14) is given by:

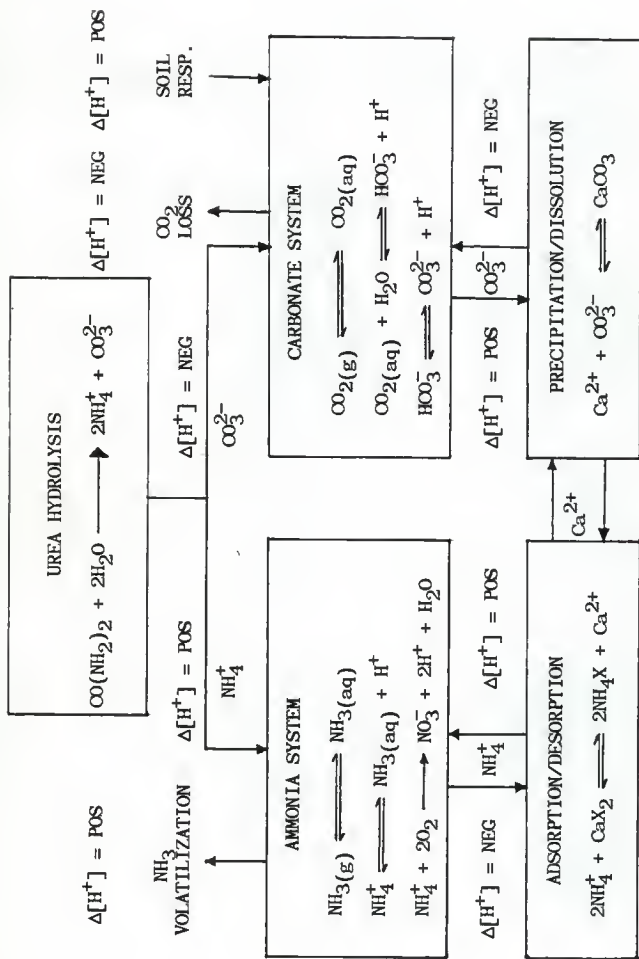


Figure 1-1 Effect of soil equilibria on soil pH.

$$K_2 = \frac{[\text{NH}_3(\text{aq})][\text{H}^+]}{[\text{NH}_4^+]} \dots \dots \dots (1-22)$$

The quantities in brackets are the concentrations of the species in soil solution. Equation (1-22) suggests that if K_2 is to remain constant (by definition, it is constant for a given temperature), both $[\text{NH}_3(\text{aq})]$ and $[\text{H}^+]$ must increase if $[\text{NH}_4^+]$ increases. Since urea hydrolysis increases $[\text{NH}_4^+]$, it follows that $[\text{NH}_3(\text{aq})]$ and $[\text{H}^+]$ also increase. Increase in $[\text{H}^+]$ tends to decrease soil pH. For soil pH less than 7.3, the decrease in soil pH is small, because the ratio, $[\text{NH}_3(\text{aq})]/[\text{NH}_4^+]$ is small (less than, approximately, 0.01). Further, much of the NH_4^+ produced by urea hydrolysis may be adsorbed by soil as will be discussed later. Assuming that all the NH_4^+ produced remain in solution, only 1% (approximately) will be converted to $\text{NH}_3(\text{aq})$ so that the equilibrium given by equation (1-14) is satisfied. This, theoretically, results in a small decrease in soil pH. From a practical stand point, it is offset by the increase in soil pH due to the production of CO_3^{2-} . At low soil pH (less than 8.3), the CO_3^{2-} formed are almost entirely converted to HCO_3^- according to the reaction given by equation (1-8). The equilibrium constant for this reaction (K9) is given by:

$$K_9 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} \dots \dots \dots (1-23)$$

For a given temperature, since K_9 must remain constant, equation (1-23) suggests that $[\text{H}^+]$ must decrease and $[\text{HCO}_3^-]$ must increase if $[\text{CO}_3^{2-}]$ increases. This implies that the CO_3^{2-} produced by urea

hydrolysis, react with H^+ , to form HCO_3^- . The extent of this reaction depends on the value of K_9 . At soil pH less than 8.3, the ratio $[CO_3^{2-}]/[HCO_3^-]$ is less than 0.01. To maintain this ratio, approximately, 99% of the CO_3^{2-} formed must be converted to HCO_3^- . This analysis suggests that for each mole of urea hydrolyzed, approximately one mole of H^+ are removed from soil, provided, the HCO_3^- formed are not further converted to $CO_{2(aq)}$. Practically, however, the HCO_3^- formed may react with H^+ , as represented in equation (1-10), to form $CO_{2(aq)}$. The extent of this reaction is dependent on soil pH and the value of the equilibrium constant, K_8 , given by:

$$K_8 = \frac{[HCO_3^-][H^+]}{[CO_{2(aq)}]} \dots \dots \dots (1-24)$$

At pH 6.3, $[HCO_3^-]$ and $[CO_{2(aq)}]$ are about equal. Hence at this pH, approximately, 50% of HCO_3^- formed from CO_3^{2-} will be converted to $CO_{2(aq)}$. This means that an additional 0.5 moles of H^+ are removed from soil, for a total of 1.5 moles of H^+ removed per mole urea hydrolyzed. In soil, $CO_{2(g)}$ loss disturbs this equilibria, and even more H^+ are consumed from the soil.

It should be clear from the previous discussion that urea hydrolysis tends to raise the pH of soil. The effect is more pronounced at low soil pH. It should, however, be noted that soil pH is also influenced by other reactions, such as soil respiration, which tends to lower the pH. Therefore, the percentage figures given in the previous discussion should be interpreted as approximately correct, if and only if, urea hydrolysis were the sole reaction disturbing the soil equilibria.

Soil respiration is an irreversible, biochemical reaction in which aerobic soil micro-organisms utilize organic carbon (as substrate) from soil to produce carbon dioxide gas. The production of CO_2 increases the partial pressure of CO_2 in the gaseous phase. From Henry's Law, it follows that the concentration of CO_2 in the aqueous phase will increase. Once again, the carbonate system equilibria is disturbed, and a new set of equilibrium conditions must be met. This time, however, the equilibrium is approached from the opposite direction which means that the reactions given by equations (1-8) and (1-10) proceed to the right, as written. Examination of these equations reveals that the reactions can proceed to the right only if H^+ are released to soil. Therefore, soil respiration tends to lower the pH.

The effect of NH_4^+ adsorption by soil will now be discussed. Adsorption of NH_4^+ disturbs the equilibrium between NH_4^+ and $\text{NH}_3(\text{aq})$. It is clear from equation (1-22) that if $[\text{NH}_4^+]$ decreases, both $[\text{NH}_3(\text{aq})]$ and $[\text{H}^+]$ must decrease to meet the condition that K_2 remain constant for a given temperature. Therefore, adsorption of NH_4^+ tends to increase the pH of soil. Conversely, desorption of NH_4^+ tends to decrease the soil pH.

Adsorption of NH_4^+ proceeds with release of calcium ions (Ca^{2+}) into soil solution as indicated by equation (1-15). Therefore Ca^{2+} concentration increases in soil solution and remains in equilibrium with $\text{CaCO}_3(\text{s})$ as represented by equation (1-9). The solubility product of Ca^{2+} and CO_3^{2-} is given by:

$$K_{11} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] \dots \dots \dots (1-25)$$

As noted earlier, below pH 8.3, urea hydrolysis proceeds with a negligible increase in $[\text{CO}_3^{2-}]$. Therefore, the major factor for calcium carbonate $[\text{CaCO}_{3(s)}]$ precipitation is the increase in $[\text{Ca}^{2+}]$ due to adsorption of NH_4^+ . Equation (1-25) suggests that when the product of $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ exceeds K_{11} , $\text{CaCO}_{3(s)}$ will precipitate. Since CO_3^{2-} are removed from soil solution when $\text{CaCO}_{3(s)}$ precipitates, the equilibrium between HCO_3^- and CO_3^{2-} , given by equation (1-23) is disturbed. It follows from equation (1-23) that for K_9 to remain constant, $[\text{HCO}_3^-]$ must decrease and $[\text{H}^+]$ must increase if $[\text{CO}_3^{2-}]$ decreases. This is possible if equation (1-8) as written, proceeds to the right i.e. HCO_3^- dissociate to H^+ and CO_3^{2-} . Therefore, precipitation of $\text{CaCO}_{3(s)}$ tends to resist a rise in soil pH through release of H^+ . When NH_4^+ are desorbed, Ca^{2+} are removed from soil solution by adsorption. Removal of Ca^{2+} decreases the product of $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$, and as a result, $\text{CaCO}_{3(s)}$ dissolution occurs until the equilibrium given by equation (1-25) is satisfied. Therefore, dissolution of $\text{CaCO}_{3(s)}$ tends to increase soil pH owing to its effect on the equilibrium between HCO_3^- and CO_3^{2-} .

Next the effect of $\text{CO}_{2(g)}$ loss and $\text{NH}_{3(g)}$ loss from the soil surface will be considered. $\text{CO}_{2(g)}$ loss tends to raise the soil pH while $\text{NH}_{3(g)}$ loss tends to lower it. Loss of $\text{CO}_{2(g)}$ decreases the concentration of $\text{CO}_{2(g)}$ in the soil air of the surface layer of soil. This disturbs the equilibrium between $\text{CO}_{2(g)}$ and $\text{CO}_{2(aq)}$, represented by equation (1-5). The Henry's Law constant for the equilibrium between $\text{CO}_{2(g)}$ and $\text{CO}_{2(aq)}$ is given by:

$$K_7 = \frac{[\text{CO}_{2(\text{aq})}]}{[\text{CO}_{2(\text{g})}]} \dots \dots \dots (1-5a)$$

Clearly, if $[\text{CO}_{2(\text{g})}]$ decreases, $[\text{CO}_{2(\text{aq})}]$ must decrease to keep K_7 constant. This is possible if carbon dioxide is released from the aqueous to the gaseous phase i.e. equation (1-5), as written, proceeds to the left. Decrease in $[\text{CO}_{2(\text{aq})}]$ affects the equilibria between $\text{CO}_{2(\text{aq})}$ and HCO_3^- and between HCO_3^- and CO_3^{2-} . In each case, H^+ are consumed in order to reestablish equilibrium. Hence it may be concluded that $\text{CO}_{2(\text{g})}$ loss tends to raise soil pH.

In a similar way, ammonia volatilization decreases ammonia gas concentration in the soil air of the surface layer of soil. From Henry's Law, it follows that $[\text{NH}_{3(\text{aq})}]$ must decrease, and this decrease in turn affects the equilibrium between $\text{NH}_{3(\text{aq})}$ and NH_4^+ . From equation (1-22), it is clear that $[\text{NH}_4^+]$ must decrease to reestablish equilibrium. Thus some NH_4^+ are converted to $\text{NH}_{3(\text{aq})}$, releasing H^+ as given by equation (1-14). Therefore, ammonia volatilization tends to lower the soil pH.

Quantitative Analysis for Soil pH

In the previous discussion regarding the effect of processes on soil pH, each process was characterized by its tendency to either raise or to lower the soil pH. For example, urea hydrolysis was characterized as tending to raise the soil pH. Since in practice these processes occur simultaneously, it is not possible to predict the net effect of these processes on soil pH in a qualitative manner.

Therefore, the effect of the simultaneous occurrence of these processes on soil pH will be determined, quantitatively.

The fundamental assumption in the quantitative analysis that follows is that the ratio of the change in concentration of one species to the change in concentration of a second species is equal to the partial derivative (in terms of concentration) of the first species with respect to the second species. Mathematically, this assumption is given by:

$$\frac{\Delta[\text{species}, i]}{\Delta[\text{species}, j]} = \frac{\partial[\text{species}, i]}{\partial[\text{species}, j]} \dots \dots \dots (1-26)$$

In equation (1-26), the symbol Δ represents change, in time interval DT , and the quantity within brackets represents concentration. The symbol, ∂ , represents a partial change. The variables used in the analysis are defined as follows:

- UHYD = urea hydrolyzed, kmol/m^3 soil sol
- CPPT = calcium carbonate precipitated, kmol/m^3 soil sol
- CLOS = $\text{CO}_{2(g)}$ loss from soil surface, kmol/m^3 soil air
- NLOS = $\text{NH}_{3(g)}$ loss from soil surface, kmol/m^3 soil air
- RESP = $\text{CO}_{2(g)}$ respired, kmol/m^3 soil air
- ADSB = NH_4^+ adsorbed, kmol/m^3 soil sol
- X = CO_3^{2-} converted to HCO_3^- , kmol/m^3 soil sol
- Y = HCO_3^- converted to $\text{CO}_{2(aq)}$, kmol/m^3 soil sol
- Z = $\text{CO}_{2(aq)}$ converted to $\text{CO}_{2(g)}$, kmol/m^3 soil sol
- T = NH_4^+ converted to $\text{NH}_{3(aq)}$, kmol/m^3 soil sol
- R = $\text{NH}_{3(aq)}$ converted to $\text{NH}_{3(g)}$, kmol/m^3 soil sol

K1 = equilibrium constant for equation (1-11), defined to be equal to $[\text{NH}_3(\text{aq})]/[\text{NH}_3(\text{g})]$

K7 = equilibrium constant given by equation (1-5a), and defined to be equal to $[\text{CO}_2(\text{aq})]/[\text{CO}_2(\text{g})]$

$$P12 = \partial[\text{CO}_3^{2-}]/\partial[\text{HCO}_3^-]$$

$$P11 = \partial[\text{CO}_2(\text{aq})]/\partial[\text{HCO}_3^-]$$

$$P5 = \partial[\text{NH}_3(\text{aq})]/\partial[\text{NH}_4^+]$$

The change in concentration of the various species in time

interval, DT seconds is as follows:

$$\Delta[\text{CO}_3^{2-}] = (\text{UHYD} - \text{CPPT} - \text{X}), \text{ kmol/m}^3 \text{ soil sol}$$

$$\Delta[\text{HCO}_3^-] = (\text{X} - \text{Y}), \text{ kmol/m}^3 \text{ soil sol}$$

$$\Delta[\text{CO}_2(\text{aq})] = (\text{Y} - \text{Z}), \text{ kmol/m}^3 \text{ soil sol}$$

$$\Delta[\text{CO}_2(\text{g})] = (\text{RESP} - \text{CLOS} + \frac{\text{Z}}{\text{K7}}), \text{ kmol/m}^3 \text{ soil air}$$

$$\Delta[\text{NH}_4^+] = (2 \text{ UHYD} - \text{ADSB} - \text{T}), \text{ kmol/m}^3 \text{ soil sol}$$

$$\Delta[\text{NH}_3(\text{aq})] = (\text{T} - \text{R}), \text{ kmol/m}^3 \text{ soil sol}$$

$$\Delta[\text{NH}_3(\text{g})] = (\frac{\text{R}}{\text{K1}} - \text{NLOS}), \text{ kmol/m}^3 \text{ soil air}$$

Application of equation (1-26) gives:

$$\frac{\Delta[\text{CO}_3^{2-}]}{\Delta[\text{HCO}_3^-]} = \frac{\partial[\text{CO}_3^{2-}]}{\partial[\text{HCO}_3^-]}$$

$$\text{or: } \frac{(\text{UHYD} - \text{CPPT} - \text{X})}{\text{X} - \text{Y}} = P12$$

Simplifying:

$$\text{X} = \frac{(\text{UHYD} - \text{CPPT}) + P12\text{Y}}{(1 + P12)} \dots \dots \dots (1-27)$$

$$\text{From equation (1-26): } \frac{\Delta[\text{CO}_{2(\text{aq})}]}{\Delta[\text{HCO}_3^-]} = \frac{\partial[\text{CO}_{2(\text{aq})}]}{\partial[\text{HCO}_3^-]}$$

$$\text{or: } \frac{Y - Z}{X - Y} = P11$$

Simplifying:

$$Z = Y(1 + P11) - P11 X \quad \dots \dots \dots (1-28)$$

$$\text{From equation (1-26): } \frac{\Delta[\text{CO}_{2(\text{aq})}]}{\Delta[\text{CO}_{2(\text{g})}]} = \frac{\partial[\text{CO}_{2(\text{aq})}]}{\partial[\text{CO}_{2(\text{g})}]}$$

$$\text{or: } \frac{Y - Z}{\frac{K7(\text{RESP} - \text{CLOS})}{K7} + Z} = K7$$

Simplifying:

$$Z = \frac{Y + K7(\text{CLOS} - \text{RESP})}{2} \quad \dots \dots \dots (1-29)$$

$$\text{From equation (1-26): } \frac{\Delta[\text{NH}_{3(\text{aq})}]}{\Delta[\text{NH}_4^+]} = \frac{\partial[\text{NH}_{3(\text{aq})}]}{\partial[\text{NH}_4^+]}$$

$$\text{or: } \frac{T - R}{(2 \text{ UHYD} - \text{ADSB} - T)} = P5$$

Simplifying:

$$T = \frac{R + P5 (2 \text{ UHYD} - \text{ADSB})}{1 + P5} \quad \dots \dots \dots (1-30)$$

$$\text{From equation (1-26): } \frac{\Delta[\text{NH}_{3(\text{aq})}]}{\Delta[\text{NH}_{3(\text{g})}]} = \frac{\partial[\text{NH}_{3(\text{aq})}]}{\partial[\text{NH}_{3(\text{g})}]}$$

$$\text{or: } \frac{T - R}{\frac{R - K1 \text{ NLOS}}{K1}} = K1$$

Simplifying:

$$T = 2R - K1 (\text{NLOS}) \dots \dots \dots (1-31)$$

Eliminating Z from equations (1-28) and (1-29) and simplifying:

$$X = \frac{Y (1 + 2 P11) - K7 (\text{CLOS} - \text{RESP})}{2 P11} \dots \dots \dots (1-32)$$

Eliminating X from equations (1-27) and (1-32) and simplifying:

$$Y = \frac{2 P11 (\text{UHYD} - \text{CPPT}) + K7(1 + P12)(\text{CLOS} - \text{RESP})}{(1 + 2 P11 + P12)} \dots (1-33)$$

Substituting equation (1-33) in equation (1-27) and simplifying:

$$X = \frac{(1 + 2 P11)(\text{UHYD} - \text{CPPT}) + K7(P12) (\text{CLOS} - \text{RESP})}{(1 + 2 P11 + P12)} \dots (1-34)$$

Eliminating T from equations (1-30) and (1-31) and simplifying:

$$R = \frac{K1 (1 + P5) \text{NLOS} + P5 (2 \text{UHYD} - \text{ADSB})}{(1 + 2 P5)} \dots \dots \dots (1-35)$$

Substituting equation (1-35) in equation (1-31) and simplifying:

$$T = \frac{K1(\text{NLOS}) + 2 P5 (2 \text{UHYD} - \text{ADSB})}{(1 + 2 P5)} \dots \dots \dots (1-36)$$

A net sink term which is incorporated in the H^+ mass balance (to be examined in the next chapter) is obtained from the following equation:

$$[H^+]_{\text{sink}} = X + Y - T \dots \dots \dots (1-37)$$

Substituting equations (1-32), (1-33) and (1-36) in equation (1-37) and simplifying:

$$[H^+]_{\text{sink}} = \frac{(\text{UHYD} - \text{CPPT})(1 + 4P11) + K7(1 + 2P12)(\text{CLOS} - \text{RESP}) - (1 + 2P11 + P12)}{(1 + 2P11 + P12)} - \frac{K1(\text{NLOS}) + 2P5(2\text{UHYD} - \text{ADSB})}{(1 + 2P5)} \dots \dots \dots (1-38)$$

Equation (1-38) is applicable to the H^+ mass balance at the soil surface. In order to apply it below the soil surface, CLOS and NLOS must be set equal to zero. UHYD is evaluated from a mass balance for urea. CLOS and CPPT are obtained from mass balances for carbonate species and Ca^{2+} , respectively. NLOS and ADSB are computed from a mass balance for ammoniacal species. The value of RESP depends on the type of soil (organic carbon content) and the concentration of oxygen in soil. For the present research the value of RESP was taken to be the experimentally measured value (Singh and Nye, 1986) for a sandy loam soil. This value was decreased exponentially with depth. As mentioned earlier, the Henry's Law constant, K1 and K7, for ammonia and carbon dioxide, respectively, were obtained as functions of temperature. The values of P5, P11 and P12 were obtained as follows:

$$\text{From equation (1-22): } \frac{\partial[NH_3(aq)]}{\partial[NH_4^+]} = \frac{K2}{[H^+]} = P5 \quad \dots \dots (1-39)$$

$$\text{From equation (1-23): } \frac{\partial[CO_3^{2-}]}{\partial[HCO_3^-]} = \frac{K9}{[H^+]} = P12 \quad \dots \dots (1-40)$$

$$\text{From equation (1-24): } \frac{\partial[CO_2(aq)]}{\partial[HCO_3^-]} = \frac{[H^+]}{K8} = P11 \quad \dots \dots (1-41)$$

Once again, the values of K2, K8 and K9 were obtained as functions of temperature from Hales and Drewes (1979).

In order to verify that the effect of the individual terms that comprise the $[H^+]_{sink}$ in equation (1-38), is correctly incorporated in the H^+ mass balance, it is necessary to rewrite equation (1-38) in an alternate form:

$$\begin{aligned}
[H^+]_{\text{sink}} = & \frac{(1+4P11)UHYD}{(1+2P11+P12)} + \frac{K7(1+2P12)CLOS}{(1+2P11 + P12)} + \frac{2P5 \text{ ADSB}}{(1+2P5)} \\
& - \frac{(1+4P11)CPPT}{(1+2P11+P12)} - \frac{K7(1+2P12)RESP}{(1+2P11+P12)} - \frac{K1 \text{ NLOS}}{(1+2P5)} \\
& - \frac{4P5 \text{ UHYD}}{(1+2P5)} \dots \dots \dots (1-42)
\end{aligned}$$

The first term on the right-hand side of equation (1-42) accounts for the effect of urea hydrolysis on soil pH, owing to its effect on the carbonate system equilibria. The second term accounts for the effect on soil pH due to $\text{CO}_2(\text{g})$ loss. The third term accounts for the effect of NH_4^+ adsorption or desorption on soil pH. The fourth term accounts for the effect on soil pH due to $\text{CaCO}_3(\text{s})$ precipitation or dissolution. The fifth term accounts for the effect of soil respiration on soil pH. The sixth term accounts for the effect of $\text{NH}_3(\text{g})$ loss on soil pH. The last term accounts for the effect on soil pH owing to its effect on the ammonia system equilibria. The second and sixth terms are both equal to zero for H^+ mass balance below the soil surface. The first two terms contribute toward raising the soil pH, while the fifth, sixth and the last term tend to lower the soil pH. The third term tends to raise the soil pH if ADSB is positive (adsorption occurs) and to lower the pH if ADSB is negative (desorption occurs). The fourth term tends to lower the soil pH if CPPT is positive (precipitation occurs) and to raise the pH if it is negative (dissolution occurs). These observations are consistent with the qualitative characterizations made earlier.

It is necessary to check into the units of each term of equation (1-42) and to modify them, if necessary, so that the units used in H^+

mass balance are consistent. In the present model, the variables used along with their units are as follows:

- U = urea hydrolyzed, $\text{kmol}/(\text{m}^2 \text{soil})(\text{s})$
 $UCA = \text{CaCO}_3(\text{s})$ precipitated or dissolved, $\text{kmol}/(\text{m}^2 \text{soil})(\text{s})$
 $\text{ADS} = \text{NH}_4^+$ adsorbed or desorbed, $\text{kmol}/\text{kg soil}$
 $\text{CO}_2\text{LOS} = \text{CO}_2(\text{g})$ loss from soil surface, $\text{kmol}/(\text{m}^2 \text{soil})(\text{s})$
 $\text{NH}_3\text{LOS} = \text{NH}_3(\text{g})$ loss from soil surface, $\text{kmol}/(\text{m}^2 \text{soil})(\text{s})$
 $\text{RESPIR} = \text{CO}_2(\text{g})$ respired, $\text{kmol}/(\text{m}^2 \text{soil})(\text{s})$
 WA = soil moisture content, $\text{m}^3 \text{soil sol}/\text{m}^3 \text{soil}$
 FA = air-filled soil porosity, $\text{m}^3 \text{soil air}/\text{m}^3 \text{soil}$
 VOL = specific volume of soil, $\text{m}^3 \text{soil}/\text{m}^2 \text{soil}$
 DT = time interval, s

In order to use these variables in H^+ mass balance and for the sake of dimensional consistency, equation (1-42) is modified, thus:

$$\begin{aligned}
 [\text{H}^+]_{\text{sink}} = & \frac{(1+4P11)(U)}{(1+2P11+P12)} + \frac{K7(1+2P12)(WA)(\text{CO}_2\text{LOS})}{(FA)(1+2P11+P12)} + \frac{2P5(WA)(VOL)\text{ADS}}{P6(DT)(1+2P5)} \\
 & - \frac{(1+4P11)UCA}{(1+2P11+P12)} - \frac{K1(\text{NH}_3\text{LOS})WA}{(FA)(1+2P5)} - \frac{K7(1+2P12)(WA)(\text{RESPIR})}{FA(1+2P11+P12)} \\
 & - \frac{4P5(U)}{(1+2P5)} \dots \dots \dots (1-43)
 \end{aligned}$$

The third term on the right-hand side of equation (1-43) contains a new variable, $P6$ which is defined to be:

$$P6 = \frac{\partial[\text{NH}_4^+(\text{ad})]}{\partial[\text{NH}_4^+]} = (\text{NK2})(\text{NK1})([\text{NH}_4^+])^{\text{NK2}-1} \dots \dots \dots (1-44)$$

The partial derivative of equation (1-44) was obtained from equation (1-16).

Mass Transfer in Soil

It was stated at the beginning of this chapter that ammonia volatilization is influenced to a significant degree by mass transfer processes, both in the aqueous and in the gaseous phase. Indeed, solute transport has a pronounced effect on soil equilibria and hence on ammonia volatilization. In this section of the chapter, mass transfer theory will be presented along with the development of equations used in the model to describe mass transfer of various ionic and molecular species.

In general, mass transfer occurs by three mechanisms: molecular diffusion, mechanical dispersion (hydrodynamic dispersion) and convection. In the present research, mass transfer by mechanical dispersion, is ignored. Mass transfer, by molecular diffusion, is due to a concentration gradient, while mass transfer by convection is due to the bulk motion of a fluid. In soils, convective transport occurs in response to a hydraulic potential gradient. Mechanical dispersion, in soils, may be conceptualized as the dispersion of a solute about the mean position of a moving front of soil solution, resulting in a transport rate faster than by convection and diffusion, alone.

In a uniform body of a fluid, mass transfer by diffusion is described by Fick's first law:

$$J_{A,M} = -D_{AB} \frac{\partial C_A}{\partial Z} \dots \dots \dots (1-45)$$

$J_{A,M}$ = flux of solute A in the Z-direction, $\text{kmol}/(\text{m}^2)(\text{s})$

D_{AB} = diffusion coefficient (diffusivity) of A for a solution of solute A in solvent B, m^2/s

$\frac{\partial C}{\partial Z}$ = concentration gradient of A in Z-direction, kmol/m^4

The negative sign in equation (1-45) denotes that diffusion occurs in the direction of decreasing concentration of the solute. In soils, the diffusion coefficient for a solute is less than its diffusion coefficient in a uniform body of water. This is attributed to the tortuosity of the path for diffusion and to the cross-sectional area of water available for diffusion. Papendick and Campbell (1980), proposed the following equation for diffusion in soils:

$$D_s = a D_w \theta^3 \dots \dots \dots (1-46)$$

D_s = diffusion coefficient of solute in soil, $\text{m}^3 \text{ soil sol}/(\text{m soil})(\text{s})$

D_w = diffusion coefficient of solute in uniform body of water, $\text{m}^3 \text{ soil sol}/\text{s}$

a = an empirical constant that accounts for tortuosity.

θ = water content of soil, $\text{m}^3 \text{ soil sol}/\text{m}^3 \text{ soil}$

It is worthwhile to note that in the literature (Campbell, 1985; Bresler, 1973), no units are given for the empirical constant, a . If, however, Fick's first law is used for diffusional mass transfer in soils, then D_s , given by equation (1-46), must replace D_{AB} in equation (1-45). For the sake of dimensional consistency of equation (1-45), the units of D_s must be as given earlier when the units of concentration are $\text{kmol/m}^3 \text{ soil sol}$. It follows that for equation (1-46) to be dimensionally consistent, the units of the empirical constant, a , must be:

$$\frac{\text{m soil sol}/\text{m soil}}{(\text{m}^3 \text{ soil sol}/\text{m}^3 \text{ soil})^3}$$

Thus, the factor, $\alpha\theta^3$, which has the units of (m soil sol/m soil), may be interpreted as a measure to account for both tortuosity and the cross-sectional area of water available for diffusion.

Gaseous diffusion in soils is also less than in a uniform body of a gas mixture (air). Once again, tortuosity of the path of diffusion and the cross-sectional area of soil air available for diffusion may be cited as reasons for the slower diffusion rate of a gas in soil. The following equation, proposed by Sallam et al. (1984), is used to describe gaseous diffusion in soils:

$$D_s = D_{air} \theta_g^m / \theta^2 \dots \dots \dots (1-47)$$

D_s = diffusion coefficient of gas in soil, m^3 soil air/(m soil)(s)

D_{air} = diffusion coefficient of gas in air, m^2 soil air/s

θ_g = air-filled porosity of soil, m^3 soil air/ m^3 soil

θ = total porosity of soil, dimensionless

m = an empirical constant that accounts for tortuosity

The factor, θ_g^m must have the units of (m soil air/m soil) if Fick's first law is used for gaseous diffusion in soil. For gaseous diffusion, the units of concentration gradient in equation (1-45) are $k \text{ mol}/(m^3 \text{ soil air})(m)$.

Convective mass transfer in soils is given by:

$$J_{A,C} = qC_A \dots \dots \dots (1-48)$$

$J_{A,C}$ = convective flux of solute A in the direction of soil water flux, $kmol/(m^2 \text{ soil})(s)$

q = soil water flux, $m^3 \text{ soil sol}/(m^2 \text{ soil})(s)$

C_A = concentration of solute A, $kmol/m^3 \text{ soil sol}$

The mathematical form of mass transfer by mechanical dispersion is identical to that for molecular diffusion. However, the diffusion coefficient is replaced by a dispersion coefficient. Bresler (1973) suggests that under saturated and steady flow conditions in soil, the dispersion coefficient is given by:

$$D_h = \lambda q / \theta \dots \dots \dots (1-49)$$

where q and θ are defined as for equations (1-48) and (1-46) respectively:

λ = an experimental constant, depending on the characteristics of soil, m^3 soil sol/ m^2 soil

D_h = mechanical dispersion coefficient, m^3 soil sol/(m soil)(s)

The values of λ for the various ionic and molecular species considered in the present model are not presently available. Further, equation (1-49) is applicable to saturated and steady flow conditions, while in the present model, unsaturated and unsteady flow conditions prevail. Owing to these limitations, it was considered appropriate to exclude the effect of mechanical dispersion from the overall mass transfer process which simplifies to:

$$J = - D_s \frac{\partial C}{\partial Z} + q C \dots \dots \dots (1-50)$$

Equation (1-50) is applicable to steady flow conditions which seldom prevail under field conditions. Hence it is necessary to develop an equation which describes mass transfer under unsteady flow conditions. Such an equation may be derived from the Equation of Continuity. A general form of this equation is:

$$\begin{aligned} \left[\begin{array}{c} \text{Rate of Mass} \\ \text{Accumulation} \end{array} \right] &= \left[\begin{array}{c} \text{Rate of Mass} \\ \text{In} \end{array} \right] - \left[\begin{array}{c} \text{Rate of Mass} \\ \text{Out} \end{array} \right] + \left[\begin{array}{c} \text{Rate of Mass} \\ \text{Production} \end{array} \right] \\ &- \left[\begin{array}{c} \text{Rate of Mass} \\ \text{Consumption} \end{array} \right] \dots \dots \dots (1-51) \end{aligned}$$

For one-dimensional mass transfer in soils, the Equation of Continuity for a solute is given by (Bresler, 1973):

$$\frac{\partial}{\partial t} (Q + \theta C) = \frac{\partial}{\partial Z} [D(v, \theta) \frac{\partial C}{\partial Z}] - \frac{\partial (qC)}{\partial Z} \pm S \dots \dots \dots (1-52)$$

where:

Z, θ , C and q are as defined for equations (1-48) through (1-50).

$D(v, \theta) = (D_s + D_h)$, D_s and D_h given by equations (1-46) and

(1-49), respectively, $m^3 \text{ soil sol}/(m \text{ soil})(s)$

S = any sink or source rate term, $kmol/(m^3 \text{ soil})(s)$

Q = solute concentration in the adsorbed phase, $kmol/m^3 \text{ soil}$

t = time, s.

The units of each term in equation (1-52) are $k \text{ mol}/(m^3 \text{ soil})(s)$.

Hence, equation (1-52) represents an unsteady-state mass balance, on a molar basis. A comparison of equations (1-51) and (1-52) reveals that:

$$\frac{\partial}{\partial t} (Q + \theta C) = \text{Rate of mass accumulation}$$

$$\frac{\partial}{\partial Z} [D(v, \theta) \frac{\partial C}{\partial Z}] - \frac{\partial (qC)}{\partial Z} = (\text{Rate of mass in}) - (\text{Rate of mass out})$$

$$S = (\text{Rate of mass production}) - (\text{Rate of mass consumption})$$

The second-order finite difference approximation to the partial differential equation [equation (1-52)] is given by Bresler (1973).

The finite differencing scheme proposed by Bresler (1973) is a Crank-Nicholson scheme which is second-order accurate in time and space. The scheme used in this research is similar to the one proposed by Campbell (1985). One significant difference between the approach undertaken in this research and the one proposed by Campbell (1985) lies in the method used to account for the convection term in equation (1-52). A second difference may be attributed to how the diffusion coefficients are averaged in space. In this research, the diffusion coefficients are averaged in space as proposed by Press et al. (1986). Campbell (1985) does not specify how the diffusion coefficients are to be averaged. One disadvantage of the scheme proposed by Campbell (1985) is that it is only first-order accurate in time and space. Since the Crank-Nicholson scheme is expected to provide more accurate results than a first-order accurate scheme, it is recommended that for further research into improving the present model, the Crank-Nicholson scheme be used.

In the present model, the finite difference approximation to equation (1-52) is given by:

$$\begin{aligned} & \frac{\Delta Z}{\Delta t} [(Q_1^{n+1} - Q_1^n) + \bar{\theta}_1 (C_1^{n+1} - C_1^n)] \\ & = \frac{\bar{D}_{i+1/2}(\bar{C}_{i+1} - \bar{C}_i) - \bar{D}_{i-1/2}(\bar{C}_i - \bar{C}_{i-1})}{\Delta Z} \\ & + \bar{N}_1 \pm S_1^{n+1} \dots \dots \dots (1-53) \end{aligned}$$

In equation (1-53) subscript, i designates space (the total soil depth is divided into a finite number of nodes, each node located at a given

depth) while superscript, n denotes time. For example, C_i^{n+1} implies the concentration of a species at node i and at a time, (n+1). The diffusion coefficient, $\bar{D}_{i+1/2}$ is defined by:

$$\bar{D}_{i+1/2} = 1/2 (\bar{D}_i + \bar{D}_{i+1}) \dots \dots \dots (1-54)$$

Similarly, $\bar{D}_{i-1/2}$ is given by:

$$\bar{D}_{i-1/2} = 1/2 (\bar{D}_{i-1} + \bar{D}_i) \dots \dots \dots (1-55)$$

The term, $\bar{N}_i$, in equation (1-53), accounts for the convective term in equation (1-52). The details of its computation will be explained in the next chapter where major improvements to the model, made as part of this research, will be discussed. For the present understanding, it may be helpful to consider that the computation of $\bar{N}_i$ involves a mass balance approach, which takes into account, the direction of soil water flux. The term, S_i^{n+1} is a source-sink term. ΔZ , $\bar{\theta}_i$ and $\bar{C}_i$ are defined by the following equations:

$$\Delta Z = Z_{i+1} - Z_i \dots \dots \dots (1-56)$$

$$\bar{\theta}_i = \eta \theta_i^{n+1} + (1-\eta) \theta_i^n \dots \dots \dots (1-57)$$

$$\bar{C}_i = \eta C_i^{n+1} + (1-\eta) C_i^n \dots \dots \dots (1-58)$$

In equation (1-56) and (1-57), η is a weighting factor in time (Campbell, 1985). The values of η may range from 0 to 1. The numerical procedure in which η is set equal to zero is called an explicit scheme because values for the new time step are solved explicitly from the values of the previous time step. If η is equal to 1, the resulting numerical technique is a fully implicit scheme. In the fully implicit scheme, the values for the new time step are determined from assumed values for the new time step. The numerical procedure in

which η is set equal to 0.5, is referred to by Campbell (1985) as the Crank-Nicholson procedure. Strictly speaking, however, the finite difference equations for the Crank-Nicholson scheme developed by Bressler (1973) are more elaborate and more complicated than those obtained by setting η equal to 0.5. Stable solutions of equation (1-53) are assured if η is greater than 0.5 (Campbell, 1985). In the next section of this chapter, the numerical method used to solve equation (1-53) is explained.

Development of General Mass Balance Equation

Equation (1-53), as written, is applicable to the mass balance for individual chemical species, such as, NH_4^+ , HCO_3^- , Ca^{2+} , H^+ . Therefore, in the model developed for this research, mass balances for Ca^{2+} and H^+ may be represented by an equation of the form of equation (1-53). However, equation (1-53) does not completely represent lumped mass balances for ammoniacal and carbonate species. In the present model, the mass balance for all ammoniacal species is incorporated into one equation which, in effect, represents a nitrogen balance (N-balance). Similarly, the mass balance for all carbonate species is lumped into a single equation, which effectively is a carbon balance (C-balance). A general equation which represents all mass balances made in the model is as follows:

$$\frac{\Delta Z}{\Delta t} \left[\sum_{l=1}^j \bar{\theta}_i \bar{p}_{l,i} (C_i^{n+1} - C_i^n) + \rho_{b,i} \bar{p}_{s,i} (C_i^{n+1} - C_i^n) + \bar{\theta}_{g,i} \bar{p}_{g,i} (C_i^{n+1} - C_i^n) \right] = \frac{\bar{D}_{i+1/2}}{Z_{i+1} - Z_i} (\bar{C}_{i+1} - \bar{C}_i) - \frac{\bar{D}_{i-1/2}}{Z_i - Z_{i-1}} (\bar{C}_i - \bar{C}_{i-1}) + \bar{N}_i \pm S_i^{n+1} \dots \dots \dots (1-59)$$

The term, $\bar{\theta}_i \bar{p}_{l,i} (C_i^{n+1} - C_i^n)$ is summed for $l = 1$ to j where:

j = total number of ammoniacal species in solution (for N-balance) or total number of carbonate species in solution (for C-balance). For the mass balances of Ca^{2+} and urea, j is unity, while, for the H^+ mass balance, j is equal to two.

The other variables in equation (1-59) are defined as follows:

$\rho_{b,i}$ = bulk density of soil for node i , $\text{kg soil/m}^3 \text{ soil}$

$\bar{\theta}_{g,i}$ = weighted average air-filled porosity for node i during time step $n+1$, $\text{m}^3 \text{ soil air/m}^3 \text{ soil}$

$\bar{p}_{s,i}$ = partial derivative of the concentration of a species in the adsorbed phase with respect to $\bar{C}_i$ for node i , $(\text{kmol})(\text{kg soil}^{-1})/(\text{kmol})(\text{m}^3 \text{ soil sol})^{-1}$

$\bar{p}_{g,i}$ = partial derivative of the concentration of a species in soil air with respect to $\bar{C}_i$ for node i , $(\text{kmol})(\text{m}^3 \text{ soil air})^{-1}/(\text{kmol})(\text{m}^3 \text{ soil sol})^{-1}$

$\bar{P}_{1,i}, \bar{P}_{2,i} \dots \bar{P}_{j,i}$ = partial derivatives of the concentrations of species in the soil sol with respect to C_i for node i , $(\text{kmol})(\text{m}^3 \text{ soil air})^{-1}/(\text{kmol})(\text{m}^3 \text{ soil sol})^{-1}$

$\bar{C}_i$ = average concentration of NH_4^+ (for N-balance), HCO_3^- (for C-balance), Ca^{2+} for Ca^{2+} - balance and H^+ for H^+ - balance evaluated for node i during time step $(n+1)$.

C_i^{n+1}, C_i^n = concentrations of $\text{NH}_4^+, \text{HCO}_3^-, \text{Ca}^{2+}, \text{H}^+$, as applicable, at the end of time steps $(n+1)$ and n , respectively, for node i .

If $(C_i^{n+1} - C_i^n)$ is factored from the left-hand side of equation (1-59), the resulting equation is:

$$\frac{\Delta Z}{\Delta t} \left[\sum_{i=1}^j \bar{\theta}_i \bar{P}_{1,i} + b_{s,i} \bar{P}_{s,i} + \bar{\theta}_{g,i} \bar{P}_{g,i} \right] (C_i^{n+1} - C_i^n) = \frac{\bar{D}_{i+1/2}}{Z_{i+1} - Z_i} (\bar{C}_{i+1} - \bar{C}_i) - \frac{\bar{D}_{i-1/2}}{Z_i - Z_{i-1}} (\bar{C}_i - \bar{C}_{i-1}) + \bar{N}_i \pm S_i^{n+1} \dots (1-60)$$

Equation (1-60) is a general equation, applicable to the mass balance for all chemical species in the model. The expression in brackets, on the left-hand side of equation (1-60), multiplied by $(\Delta Z/\Delta t)$, is referred to as the capacity term in the model and assigned the name CAP(I). The other variables in equation (1-60) will now be defined.

Ammoniacal Species Balance (N-Balance)

For the N-Balance, the term, $\bar{\theta}_i \cdot \bar{P}_{1,i}$ in equation (1-60) is summed for 4 species ($j=4$), namely, $\text{NH}_4^+, \text{NH}_3(\text{aq}), \text{NH}_4\text{CO}_3^-$ and $\text{NH}_4\text{HCO}_3^0$. The various $\bar{P}_{1,i}$ values are defined thus:

$$\bar{P}_{1,i} = \frac{\partial [\text{NH}_4^+]_i}{\partial [\text{NH}_4^+]_i} = 1$$

$$\bar{P}_{2,i} = \frac{\partial [\text{NH}_3(\text{aq})]_i}{\partial [\text{NH}_4^+]_i}$$

$$\bar{P}_{3,i} = \frac{\partial [\text{NH}_4\text{CO}_3^-]_i}{\partial [\text{NH}_4^+]_i}$$

$$\bar{P}_{4,i} = \frac{\partial [\text{NH}_4\text{HCO}_3^0]_i}{\partial [\text{NH}_4^+]_i}$$

The first term in brackets, on the left-hand side of equation (1-59), represents the change in N in soil solution for node i, during time step, (n+1). The second term in brackets, on the left-hand side of equation (1-59), represents the change in N in the adsorbed phase, for node i, during time step (n+1). In equation (1-53), this change was denoted by $(Q_i^{n+1} - Q_i^n)$. The variable $\bar{P}_{s,i}$ in the second term of equation (1-59) is defined by:

$$\bar{P}_{s,i} = \frac{\partial [\text{NH}_4^+(\text{ad})]_i}{\partial [\text{NH}_4^+]_i}$$

The third term in brackets, on the left-hand side of equation (1-59), represents the change in N, in soil air, for node i, during time step (n+1). The variable, $\bar{P}_{g,i}$, in the third term of equation (1-59) is defined by:

$$\bar{P}_{g,i} = \frac{\partial [\text{NH}_3(\text{g})]_i}{\partial [\text{NH}_4^+]_i}$$

The diffusion coefficients, $D_{i-1/2}$ and $D_{i+1/2}$, in equation (1-60) represent the lumped diffusivity for all ammoniacal species, for node (i-1) and node i, respectively. These diffusivities may therefore be

interpreted as the effective diffusivity of N. A general equation for the definition of $\bar{D}_{i-1/2}$ is:

$$\bar{D}_{i-1/2} = \frac{1}{2} [(\bar{P}_{g,i} \bar{D}_{g,i} + \sum_{l=1}^j \bar{P}_{l,i} \bar{D}_{l,i}) + (\bar{P}_{g,i-1} \bar{D}_{g,i-1} + \sum_{l=1}^j \bar{P}_{l,i-1} \bar{D}_{l,i-1})] \quad (1-61)$$

For N-balance, the $\bar{D}_{l,i}$ values are the diffusivities of NH_4^+ , $\text{NH}_3(\text{aq})$, NH_4CO_3^- and $\text{NH}_4\text{HCO}_3^0$ ($j=4$) for node i . $\bar{D}_{g,i}$ represents the diffusivity of $\text{NH}_3(\text{g})$ in soil air. $\bar{D}_{l,i-1}$ and $\bar{D}_{g,i-1}$ represent values corresponding to $\bar{D}_{l,i}$ and $\bar{D}_{g,i}$ for node $(i-1)$. Replacement of subscript i by $i+1$, in equation (1-61), yields the expression for $\bar{D}_{i+1/2}$.

The term $\bar{N}_i$, in equation (1-60), will be derived in Chapter 2 where major changes made in the development of the PC model are explained. For N-balance, $\bar{N}_i$ represents the net convective flux of N for node i , resulting from the convective transport of NH_4^+ and $\text{NH}_3(\text{aq})$. Since $\bar{N}_i$ may compute to be a positive quantity or a negative quantity, depending on the direction of soil water fluxes for nodes $i-1$, i and $i+1$, it may be considered as a source or a sink term in N-balance. The term, S_i^{n+1} is a source term in N-balance for all nodes below the soil surface ($i > 1$). The source of N is the urea hydrolyzed for time step $n+1$. At the surface, the mass balance is modified to account for the loss of N due to ammonia volatilization. Thus for the surface node, S_1^{n+1} is given by:

$$S_1^{n+1} = 2U_1 - N_{\text{loss}}$$

where: U_1 = urea hydrolysis rate for surface node;

N_{loss} = ammonia volatilization loss

Carbonate Species Balance (C-Balance)

For the C-Balance, the term, $\bar{\theta}_i \bar{P}_{1,i}$ is summed for 5 species ($j=5$), namely, HCO_3^- , $\text{CO}_{2(\text{aq})}$, CO_3^{2-} , NH_4CO_3^- and $\text{NH}_4\text{HCO}_3^0$. The $\bar{P}_{1,i}$ values are defined by:

$$\bar{P}_{1,i} = \partial[\text{HCO}_3^-]_i / \partial[\text{HCO}_3^-]_i = 1$$

$$\bar{P}_{2,i} = \partial[\text{CO}_3^{2-}]_i / \partial[\text{HCO}_3^-]_i$$

$$\bar{P}_{3,i} = \partial[\text{CO}_3^{2-}]_i / \partial[\text{HCO}_3^-]_i$$

$$\bar{P}_{4,i} = \partial[\text{NH}_4\text{CO}_3^-]_i / \partial[\text{HCO}_3^-]_i$$

$$\bar{P}_{5,i} = \partial[\text{NH}_4\text{HCO}_3^0]_i / \partial[\text{HCO}_3^-]_i$$

The term $\bar{P}_{s,i}$ is not defined for C-balance. For the change in the gaseous phase, $\bar{P}_{g,i}$ is defined by:

$$\bar{P}_{g,i} = \frac{\partial[\text{CO}_{2(\text{g})}]}{\partial[\text{HCO}_3^-]}$$

The diffusion coefficient, $\bar{D}_{i-1/2}$ is defined by equation (1-61). The $\bar{D}_{1i}$ values, in this case, are the diffusivities of HCO_3^- , $\text{CO}_{2(\text{aq})}$, CO_3^{2-} , $\text{NH}_4\text{HCO}_3^0$ and $\text{NH}_4\text{HCO}_3^-$. It should be noted that the diffusivities for NH_4CO_3^- and $\text{NH}_4\text{HCO}_3^0$ remain unchanged for either of the two mass balances. The term, $D_{g,i}$ represents the diffusivity of $\text{CO}_{2(\text{g})}$ in soil air for node i . Once again, $\bar{D}_{1,i-1}$ and $\bar{D}_{g,i-1}$ are the corresponding values for node $i-1$. $\bar{D}_{i+1/2}$ is obtained from equation (1-61) by replacing i by $i+1$. The term, $\bar{N}_i$, for C-balance, represents the net convective flux due to the convective transport of HCO_3^- , $\text{CO}_{2(\text{aq})}$ and CO_3^{2-} . The term, S_1^{n+1} for the surface node is given by:

$$S_1^{n+1} = U_1 - C_{\text{loss}}$$

where C_{loss} is $\text{CO}_{2(\text{g})}$ loss from soil surface and U_1 is as defined earlier.

For all other nodes, S_i^{n+1} is simply equal to U_i .

Calcium Balance (Ca^{2+} - balance)

For Ca^{2+} - balance, the term $\bar{\theta}_i \bar{P}_{1,i}$ is defined only for $l=1$.

This leads to:

$$\bar{P}_{1,i} = \frac{\partial[\text{Ca}^{2+}]_i}{\partial[\text{Ca}^{2+}]_1} = 1$$

The term $\rho_{b,i} \bar{P}_{s,i}$ is also not defined for Ca^{2+} - balance. Strictly speaking, Ca^{2+} are adsorbed and therefore $\rho_{b,i} \bar{P}_{s,i}$ exists. Since no direct relationship between Ca^{2+} and $\text{Ca}^{2+}_{(\text{ad})}$ is used in the model (as mentioned earlier, a Capon-type of equation which directly relates $[\text{Ca}^{2+}]$ to $[\text{Ca}^{2+}_{(\text{ad})}]$ was not used in this model), it is not possible to evaluate the partial derivative, $\partial[\text{Ca}^{2+}_{(\text{ad})}]/\partial[\text{Ca}^{2+}]$. Hence, the change in $[\text{Ca}^{2+}_{\text{ad}}]$ is computed from stoichiometry — 0.5 moles of Ca^{2+} are desorbed for each mole of NH_4^+ adsorbed, and vice-versa. The effect of Ca^{2+} adsorption or desorption on the mass balance is incorporated in the source/sink term, S_i^{n+1} , into which is also incorporated, the effect of $\text{CaCO}_{3(s)}$ precipitation or dissolution. Thus, the source/sink term for Ca^{2+} - balance is defined to be:

$$S_i^{n+1} = 0.5 \rho_{b,i} \bar{P}_{s,i} (C_i^{n+1} - C_i^n) - R_i$$

where $\bar{P}_{s,i}$, C_i^n and C_i^{n+1} are as defined for N-balance. The term, R_i represents $\text{CaCO}_{3(s)}$ precipitation or dissolution. As incorporated in the equation, above, R_i appears to be a sink term. This is true if precipitation of $\text{CaCO}_{3(s)}$ occurs. For dissolution of $\text{CaCO}_{3(s)}$, R_i computes as a negative quantity. Since a negative sign precedes R_i in

the equation, above, it is obvious that the effect of R_i on Ca^{2+} mass balance will be as a source term. The computation of R_i will be discussed in Chapter 2 where major changes made in the development of the PC model are discussed. The term $\theta_{g,i}^- \bar{P}_{g,i}$ in equation (1-60) does not exist for Ca^{2+} mass balance for the simple reason that none of the calcium species exist in the gaseous phase. The diffusion coefficients $\bar{D}_{i-1/2}$ may be obtained from equation (1-61) which simplifies to:

$$\bar{D}_{i-1/2} = 1/2 (\bar{P}_{1,i} \bar{D}_{1,i} + \bar{P}_{1,i-1} \bar{D}_{1,i-1})$$

where $\bar{P}_{1,i}$ is as defined earlier for Ca^{2+} mass balance and $D_{1,i}$ is the diffusivity of Ca^{2+} in soil solution for node i . $\bar{P}_{1,i-1}$ is defined in a similar way to $\bar{P}_{1,i}$ except that the partial derivative is evaluated for node $(i-1)$. Likewise, $\bar{D}_{1,i-1}$ is the diffusivity for node $(i-1)$.

Equation (1-60) is now examined for its application to the H^+ mass balance. In the soil solution, two ions affect the H^+ mass balance ($j=2$), namely, H^+ and OH^- . For the solid phase, it is assumed, that when H^+ are adsorbed or desorbed they do not exchange with NH_4^+ . Hence, buffering is provided by soil against a rise or fall in pH, but it is assumed that cation-exchange of H^+ and NH_4^+ does not occur. The assumption does not fully agree with the experimental data of Izaurralde et. al. (1987), who found that a stoichiometric relationship exists between titratable acidity of soil and $\text{NH}_4\text{-N}$ retention by soil. In other words, the experimental data suggest that H^+ on the cation exchange sites may indeed be replaced by NH_4^+ when desorption of H^+ occurs. Certainly, the complexity of cation-exchange processes

warrants further research into the adsorption and desorption mechanisms of H^+ , NH_4^+ and Ca^{2+} .

From a mathematical standpoint, the change in H^+ in the solid phase, for node i and for a time interval Δt , is given by:

$$(\Delta Z \rho_{b,i} \bar{P}_{s,i})(C_i^{n+1} - C_i^n)$$

where $\bar{P}_{s,i}$ is defined to be:

$$\bar{P}_{s,i} = \frac{\frac{\partial [H^+]_{(ad)}}{\partial [H^+]}}{\frac{\text{kmol } H^+ / \text{kg soil}}{\text{kmol } H^+ / \text{m}^3 \text{ soil sol}}}$$

Since a quantitative relation between H^+ in the adsorbed phase and H^+ in solution was not available directly, it was found necessary to define $\bar{P}_{s,i}$ in terms of quantities that have been experimentally determined or may be analytically obtained. Thus, $\bar{P}_{s,i}$ is defined by:

$$\bar{P}_{s,i} = \left(\frac{\partial [H^+]_{(ad)}}{\partial \text{pH}} \right) \left(\frac{\partial \text{pH}}{\partial [H^+]} \right) \dots \dots \dots (1-62)$$

The first quantity in parenthesis is a measure of soil buffering capacity, expressed on a unit mass of soil basis. The buffering capacity of soil may be determined experimentally by adding ammonium hydroxide (NH_4OH) to a 1:1 mixture (on a mass basis) of soil and soil solution and noting the pH of solution for each incremental addition of NH_4OH . This procedure is referred to as titration of soil, the details of which are given by Izaurralde (1985). From the experimental data, a plot of pH versus OH^- added (per unit mass of soil) is obtained. For a given pH, the buffering capacity of soil is the reciprocal of the slope of the plot at that pH. For the purpose of modeling, a convenient way of obtaining a relation between soil buffering

capacity and pH is to fit the data to an equation such as a polynomial. A least-squares fit of the experimental data given in the Annual Report (1985) was made as part of this research. The fitted, 3rd-order polynomial allowed computation of the quantity $\frac{\partial(\text{OH}^-)/\text{kg soil}}{\partial \text{pH}}$ as a function of pH.

In terms of the assumed mechanism of H^+ adsorption and desorption, the following relation holds:

$$\frac{\partial[\text{H}^+_{\text{(ad)}}]}{\partial \text{pH}} = - \frac{\partial(\text{OH}^-)/\text{kg soil}}{\partial \text{pH}} \dots \dots \dots (1-63)$$

The second quantity in parenthesis in equation (1-62) may be analytically computed from the definition of pH as follows:

$$\frac{\partial \text{pH}}{\partial [\text{H}^+]} = \frac{\partial(-\ln[\text{H}^+])}{\partial [\text{H}^+]} = - \frac{1}{2.303} \frac{\partial(\log[\text{H}^+])}{\partial [\text{H}^+]} = - \frac{0.4343}{[\text{H}^+]} \dots (1-64)$$

Substitution of equations (1-63) and (1-64) in (1-62) leads to:

$$\bar{P}_{s,i} = \frac{0.4343 \beta_1}{[\text{H}^+]_1} \dots \dots \dots (1-65)$$

where β_1 is the buffering capacity of soil for node i, on a unit mass of soil basis, and is given by the right-hand side of equation (1-63) $\text{kmol H}^+ / (\text{kg soil})(\Delta \text{pH})$.

Thus for the H^+ mass balance, the term $\bar{P}_{s,i}$ in equation (1-60), is computed from equation (1-65). The term $\bar{\theta}_{g,i} \bar{P}_{g,i}$ does not exist because hydrogen does not exit in the gaseous phase of soil. The term $\bar{\theta}_1 \bar{P}_{1,i}$ is summed for the two species, H^+ and OH^- ($j=2$). The two values of $\bar{P}_{1,i}$ are given by:

$$\bar{P}_{1,i} = \frac{\partial[H^+]_i}{\partial[H^+]_i} = 1$$

$$\bar{P}_{2,i} = \frac{\partial[OH^-]}{\partial[H^+]} = - \frac{K_w}{[H^+]^2}$$

where K_w is the ion product constant for water and is defined by:

$$K_w = [H^+][OH^-]$$

For H^+ mass balance, the terms, $\bar{D}_{i+1/2}$ and $\bar{D}_{i-1/2}$, represent the lumped diffusivities of H^+ and OH^- for nodes i and $(i-1)$, respectively.

Once again, equation (1-61) provides an estimate of $\bar{D}_{i-1/2}$ and replacement of i by $(i+1)$ in equation (1-61) allows computation of

$\bar{D}_{i+1/2}$. The terms, $\bar{P}_{g,i}$, $\bar{D}_{g,i}$ and $\bar{P}_{g,i-1}$, $\bar{D}_{g,i-1}$ do not exist. $\bar{D}_{1,i}$ and $\bar{D}_{2,i}$ are the diffusivities of H^+ and OH^- for node i . Similarly, $\bar{D}_{1,i-1}$ and $\bar{D}_{2,i-1}$ are the diffusivities of H^+ and OH^- for node $(i-1)$.

The term $\bar{N}_1$ represents the algebraic sum of the convective fluxes for H^+ and OH^- , for node i , and is given by:

$$\bar{N}_1 = \bar{N}_{1,H^+} - \bar{N}_{1,OH^-}$$

The source/sink term in H^+ mass balance has been discussed, in detail, earlier in this chapter. Hence, for the present discussion, only a general form of the source/sink term, S_1^{n+1} , will be given:

$$S_1 = (H_{clos} - H_{nlos} + H_{uc} - H_{un} + H_{ad} - H_{ppt} - H_{resp})_i \dots (1-66)$$

It should be understood that the first two terms on the right-hand side of equation (1-66) exist only for the surface node ($i=1$). The notation for equation (1-66) is:

$$H_{clos} = \text{effect of } CO_2(g) \text{ loss on } H^+ \text{ mass balance (defined for } i=1)$$

H_{nlos} = effect of $NH_3(g)$ loss on H^+ mass balance (defined for $i=1$)

H_{uc} = effect on H^+ mass balance owing to the effect of urea hydrolysis on carbonate system equilibria

H_{un} = effect on H^+ mass balance owing to the effect of urea hydrolysis on ammonia system equilibria

H_{ad} = effect of NH_4^+ adsorption/desorption on H^+ mass balance

H_{ppt} = effect of $CaCO_3(s)$ precipitation/dissolution on H^+ mass balance

H_{resp} = effect of soil respiration on H^+ mass balance

Urea Mass Balance

In the mass balance for urea:

$$\bar{P}_{1,i} = \frac{\partial \bar{C}_1}{\partial \bar{C}_1} = 1$$

where, $\bar{C}_1$ represents the average concentration of urea in soil solution. Since, it is assumed in the model that urea is not adsorbed, the term $\rho_{b,i} \bar{P}_{s,i}$ does not exist. Further, the term, $\bar{\theta}_{g,i} \bar{P}_{g,i}$, also does not exist because urea does not exist in the gaseous form. The term $\bar{D}_{i-1/2}$ may be computed from equation (1-61) where the terms $\bar{P}_{g,i}$, $\bar{D}_{g,i}$ and $\bar{P}_{g,i-1}$, $\bar{D}_{g,i-1}$ are zero. Similarly, $\bar{D}_{i+1/2}$ is computed from equation (1-61), with i replaced by $(i+1)$. The convective flux term, $\bar{N}_i$ is computed as explained in the next chapter. The source/sink term, S_i^{n+1} is simply the rate of urea hydrolysis and is therefore a sink term in the mass balance. The rate of urea hydrolysis is computed, for the present model, from equation (1-4).

Development of Newton-Raphson Algorithm

The units of equation (1-60) for all mass balances are $\text{kmol}/(\text{m}^2 \text{soil})(\text{s})$. The unknown in equation (1-60) is the new concentration C_i^{n+1} . Since a new concentration is required for each node of soil, and equation (1-60) may be written for each node, there are M unknowns and M equations where M is the number of nodes. Thus, a simultaneous solution of M equations for M number of new concentrations is possible. A careful examination of equation (1-60) reveals that there are more than one unknown quantities in each equation. For example, $\bar{C}_i$ is also an unknown since its value depends on the unknown concentration C_i^{n+1} , the two concentrations being related by equation (1-58).

Further, since the partial derivations, $\bar{P}_{l,i}$, $\bar{P}_{s,i}$ and $\bar{P}_{g,i}$, as well as the convective flux term, $\bar{N}_i$ are also evaluated at the applicable $\bar{C}_i$ values, therefore, these variables may also be considered as functions of C_i^{n+1} . Since equation (1-60) is non-linear, its solution requires a numerical procedure applicable to the simultaneous solution of M non-linear equations. In this research, the Newton-Raphson Method is used for the simultaneous solution of M equations. In order to implement this method, it is first necessary to rewrite equation (1-60) in an alternate form. Equation (1-58) along with the following relations are used to rewrite equation (1-60):

$$K_i = \frac{\Delta Z}{\Delta t} \left[\sum_{j=1}^J \theta_{i,j}^- \bar{p}_{1,i} + \rho_{b,i} \bar{p}_{s,i} + \theta_{g,i}^- \bar{p}_{g,i} \right]$$

$$D_i = \frac{\bar{D}_{i+1/2}}{Z_{i+1} - Z_i}$$

$$D_{i-1} = \frac{\bar{D}_{i-1/2}}{Z_i - Z_{i-1}}$$

$$\begin{aligned} F_i = & K_i (C_i^{n+1} - C_i^n) - D_i \eta C_{i+1}^{n+1} - D_i (1-\eta) C_{i+1}^n + D_i \eta C_i^{n+1} + D_i (1-\eta) C_i^n \\ & + D_{i-1} \eta C_i^{n+1} + D_{i-1} (1-\eta) C_i^n - D_{i-1} \eta C_{i-1}^{n+1} - D_{i-1} (1-\eta) C_{i-1}^n - \bar{N}_i \pm S_i^{n+1} \\ & \dots \dots \dots (1-67) \end{aligned}$$

For the solution of one non-linear equation in one unknown, the Newton-Raphson algorithm is simple. If x_0 is an approximation to the root of the equation $f(x) = 0$, then a better approximation to the root is x_1 which is given by:

$$x_1 = x_0 - \frac{f(x_0)}{f'(x_0)} \dots \dots \dots (1-68)$$

where:

$$f(x_0) = f(x) \text{ evaluated at } x = x_0$$

$$f'(x_0) = \text{derivative of } f(x) \text{ evaluated at } x = x_0$$

Rearrangement of equation (1-68) gives:

$$f'(x_0) [x_0 - x_1] = f(x_0) \dots \dots \dots (1-69)$$

Equation (1-69) is the form of the equation used to solve equation (1-67) by the Newton-Raphson Method. There is one complication, however, in the application of equation (1-69). Equation (1-67) contains three unknowns, C_{i+1}^{n+1} , C_i^{n+1} , C_{i-1}^{n+1} and, hence, the derivative on the

left-hand side of equation (1-69) must be obtained with respect to each of these unknowns. Thus, for each soil node, the required partial derivatives, obtained from equation (1-67), are the following:

$$\frac{\partial F_i}{\partial C_{i-1}^{n+1}} = -\eta D_{i-1} + J_{a,i} \dots \dots \dots (1-70)$$

$$\frac{\partial F_i}{\partial C_i^{n+1}} = K_i + \eta (D_i + D_{i-1}) + J_{b,i} \dots \dots \dots (1-71)$$

$$\frac{\partial F_i}{\partial C_{i+1}^{n+1}} = -\eta D_i + J_{c,i} \dots \dots \dots (1-72)$$

where $J_{a,i}$, $J_{b,i}$, $J_{c,i}$ are the partial derivatives of $\bar{N}_i$ with respect to C_{i-1}^{n+1} , C_i^{n+1} and C_{i+1}^{n+1} respectively.

Application of equation (1-69) to equation (1-67) yields:

$$F_i = \frac{\partial F_i}{\partial C_{i-1}^{n+1}} (C_{i-1}^{n+1} - C_{i-1}^n) + \frac{\partial F_i}{\partial C_i^{n+1}} (C_i^{n+1} - C_i^n) + \frac{\partial F_i}{\partial C_{i+1}^{n+1}} (C_{i+1}^{n+1} - C_{i+1}^n) \\ + \dots + \frac{\partial F_i}{\partial C_m^{n+1}} (C_m^{n+1} - C_m^n)$$

Similar equations may be written for node (i+1), node (i+2), ..., node M. All of these equations may be written compactly by using matrix algebra. For example, if M=4, the following equation in matrix form is obtained:

$$\begin{bmatrix} \partial F_1 / \partial C_1^{n+1} & \partial F_1 / \partial C_2^{n+1} & \partial F_1 / \partial C_3^{n+1} & \partial F_1 / \partial C_4^{n+1} \\ \partial F_2 / \partial C_1^{n+1} & \partial F_2 / \partial C_2^{n+1} & \partial F_2 / \partial C_3^{n+1} & \partial F_2 / \partial C_4^{n+1} \\ \partial F_3 / \partial C_1^{n+1} & \partial F_3 / \partial C_2^{n+1} & \partial F_3 / \partial C_3^{n+1} & \partial F_3 / \partial C_4^{n+1} \\ \partial F_4 / \partial C_1^{n+1} & \partial F_4 / \partial C_2^{n+1} & \partial F_4 / \partial C_3^{n+1} & \partial F_4 / \partial C_4^{n+1} \end{bmatrix} \begin{bmatrix} C_1^{n+1} - C_1^n \\ C_2^{n+1} - C_2^n \\ C_3^{n+1} - C_3^n \\ C_4^{n+1} - C_4^n \end{bmatrix} = \begin{bmatrix} F_1 \\ F_2 \\ F_3 \\ F_4 \end{bmatrix}$$

It should be noted that for $i=1$, $\partial F_1 / \partial C_{i-1}^{n+1}$ does not exist because C_{i-1}^{n+1} is not defined for $i=1$. Further, by substituting $i=1, 2, 3$ and 4 in equation (1-67), it may be verified that the following partial derivatives do not exist:

$$\partial F_1 / \partial C_3^{n+1}, \partial F_1 / \partial C_4^{n+1}, \partial F_2 / \partial C_1^{n+1}, \partial F_3 / \partial C_1^{n+1}, \partial F_4 / \partial C_1^{n+1}, \partial F_4 / \partial C_2^{n+1}$$

If all the partial derivatives that do not exist are replaced by zeros, the coefficient matrix becomes tridiagonal. Thus the resulting system of equations may be solved using the Thomas algorithm which involves a Gauss elimination scheme for the solution of the equations. As a first approximation, the C_i^{n+1} values are assumed equal to C_i^n values, so that the partial derivatives and F_i values are computed at C_i^n values. The Thomas algorithm allows computation of the C_i^{n+1} values. For a new iteration of calculations, the partial derivatives and F_i values are evaluated at the C_i^{n+1} values computed in the previous iteration. Once again, a new set of C_i^{n+1} values is obtained by application of the Thomas algorithm. This procedure is repeated until one of the following criteria are met:

$$(a) \quad 100 \left| \frac{\Sigma F_{i,j} - \Sigma F_{i,j-1}}{\Sigma F_{i,j}} \right| < 0.5 \times 10^{-2-P}$$

where:

$\Sigma F_{i,j}$ and $\Sigma F_{i,j-1}$ represent the summation of F_i values for the present iteration and previous iteration, respectively.

p is the desired accuracy of results in terms of number of significant figures

$$(b) \quad \Sigma F_{i,j} = 0$$

$$(c) \quad F_{i,j} = 0$$

In this research, criterion (b) is used for the computation of temperature and soil water content for a new time step. Criterion (a) is used for computation of new urea concentrations, while criterion (c) is used for all other mass balances.

Before this chapter is concluded, it is worthwhile to look into the stability criterion for the implicit finite differencing scheme used to solve the partial differential equations describing mass transfer by diffusion. The applicable stability criterion, given by Press et al. (1986) is:

$$\Delta t \leq \left[\frac{(\Delta Z)^2}{2D_{i+1/2}} \right]_{\min.i}$$

The equivalent stability criterion for heat transfer is given by (Simonson, 1975):

$$\Delta t < \frac{(\Delta Z)^2}{2\alpha}$$

α is the thermal diffusivity of soil, defined by:

$$\alpha = \frac{\gamma}{C_h}$$

where:

γ = thermal conductivity of soil, W/(m)(K)

C_h = volumetric heat capacity of soil, J/(m³)(K)

By a trial and error process, it was determined that the model developed for this research remained stable for:

$$\Delta t \leq 300 \text{ s}$$

CHAPTER 2

MODEL DEVELOPMENT AND DESCRIPTION

This chapter describes the development of a Personal Computer (PC) Model for simulation of ammonia volatilization under field conditions. The chapter also contains a description of how the model works. The development work may be divided into four stages. In the first stage, programming changes were made in the model existing prior to the initiation of this research. In the Introduction of this thesis, the model existing prior to the initiation of this research was referred to as the Combined Model. The same name will be used for subsequent references to this model. In the second stage, several trial runs of the PC Model were made. The results from the trial runs prompted changes in the structure of the model and led to the correction of the problem that was responsible for the prediction of negative urea hydrolysis by the Combined Model. The third stage involved the development of a 15-day meteorological data set spaced at 5-minute intervals. This data set is for the same period of time as the field study undertaken by McInnes et al. (1986). Additionally, in the third stage, two subroutines, namely IVALUE and DVALUE, were added to the model to verify mass balances for carbonate and ammoniacal species, as well as the mass balances for Ca^{2+} and H^+ . Further, several equations were modified and corrected and soil respiration was incorporated in soil equilibria. In the last stage, the model was tested with a complete meteorological data set. Results obtained from preliminary runs of the model with the complete data set suggested the need to include a convective mass transfer term in the mass balances for all chemical

species. This was accomplished by adding another subroutine to the model. Further, in the fourth stage, H^+ mass balance was modified so as to conform to the theory presented in Chapter 1. Finally, the model was run with a standard set of values for the input parameters and with different values for some of the parameters. The results obtained with the standard set of parameter values were compared with field results reported by McInnes et al. (1986). The other results were used in sensitivity analysis of the model. The development work will now be discussed as it progressed in the various stages.

It was stated in the Introduction of this thesis that the Combined Model was developed to run on a PDP-11 minicomputer. The programming language used in the Combined Model was FORTRAN. In order to adapt the model to a PC, the programming language used was Microsoft FORTRAN. This necessitated several changes in the computer code. The most significant change was that all dimensioned variables, with zero as the first subscript, were redimensioned with 1 as the first subscript. For example, the following statement is not permitted in Microsoft FORTRAN:

```
DIMENSION Z(0:M)
```

However, the statement that follows is considered to imply that the first subscript is 1:

```
DIMENSION Z(M)
```

This change led to the modification of those statements in the model where a dimensioned variable such as $Z(0)$ was required in calculations. For example, in the following statements, a value for $Z(0)$ is required when I is equal to 1:

DO 150 I = 1, M

$$VOL(I) = (Z(I+1) - Z(I-1))/2.0 \dots \dots \dots (2-1)$$

Since Z(0) is not permissible in Microsoft FORTRAN, the following modification in the second statement overcomes the problem:

$$VOL(I) = (Z(I+2) - Z(I))/2.0$$

This implies that the values of Z(I) are to be defined in such a way that the value of Z(0) is given by Z(1) and that of Z(1) is given by Z(2) and so on.

Further changes in the computer code involved changes in READ and WRITE statements, deletion of superfluous variables (variables defined in the Combined Model and not used in computations) and addition of new variables introduced as a consequence of the modifications and improvements outlined earlier.

In the development of equation (1-53), it was assumed that mass transfer occurs only in the vertical direction (Z-direction). This assumption may be justifiable for modeling uniform application of urea to soil surface. Hence, in order to use equation (1-53) to describe mass transfer in soils, uniform application of urea is assumed.

The solution of equation (1-53) implies that the total soil depth to be modeled is divided into a finite number of nodes, each node located at a specified distance below the soil surface. It is assumed that all equilibrium reactions occur at the nodes and that mass is transferred, either to a node or from a node. In the Combined Model, the depth associated with a node was computed from:

$$Z(I) = Z(I-1) + (0.0025)(I-1)^{1.5} \dots \dots \dots (2-2)$$

where:

$Z(I)$ = depth from soil surface, m

The subscript I was varied from 2 to M. Parameter, M was defined to be equal to the total number of nodes and was set equal to 7. $Z(1)$ was defined to be equal to zero since it represented the depth of the surface node.

In the PC Model, the nodal depths are considered to increase linearly and are given by:

$$Z(I) = Z(I-1) + DZ \dots \dots \dots (2-3)$$

where I is varied from 3 to KK. The variables, M, KK and DZ are defined as follows:

M = total number of nodes or soil depth increments

$$KK = M + 2$$

$$DZ = TDEPTH/M \dots \dots \dots (2-4)$$

where TDEPTH is the total modeled soil depth from the soil surface in meters. Both M and TDEPTH are considered to be modeling parameters. The value of M may be any integer value greater than zero but less than or equal to (L-2) where L is an arbitrarily defined integer. In the PC Model, L is the maximum value a subscript may have for a dimensioned variable which means that any dimensioned variable in the model has a maximum of L number of values. L has been arbitrarily set equal to 50. If L is changed, the source program of the model will need to be recompiled and relinked. The value of TDEPTH may be any value greater than or equal to 6 cm but less than or equal to 30 cm. For the standard set of input parameter values:

$$M = 15$$

TDEPTH = 0.15 m

Hence, from equation (2-4), $DZ = 0.01$ m

McInnes et al. (1986) report that toward the end of their field study "a considerable amount" of NH_4^+ were present in soil samples taken from the 4-10 cm depth increment. Since the total depth used in the PC Model is greater than 10 cm, it is probably adequate for simulation purposes. It should be noted that in the PC Model, both $Z(1)$ and $Z(2)$ are defined to be zero. Figure 2-1 depicts the soil profile used in the PC model.

In the Combined Model the volume associated with each node is computed from equation (2-1). In the PC Model, the volume is given by:

$$VOL(I) = Z(I+2) - Z(I+1) \dots \dots \dots (2-5)$$

where I is varied from 1 to M . The volume computed from either equation (2-1) or (2-5) is the specific volume or the volume per unit surface area. However, there is one significant difference between the PC Model and the Combined Model with regard to the location of the nodes. In the PC Model, as indicated in Figure 2-1, the total volume associated with a node is below the node. For the Combined Model, however, equations (2-1) and (2-2) suggest that, except for the surface node, the volume associated with a node is partly above the node and partly below it. Further, the volume of any given node and the distance between the given node and the node immediately below it are unequal because soil depths associated with nodes were increased exponentially. The significance of this difference will be evident from an examination of equation (1-60).

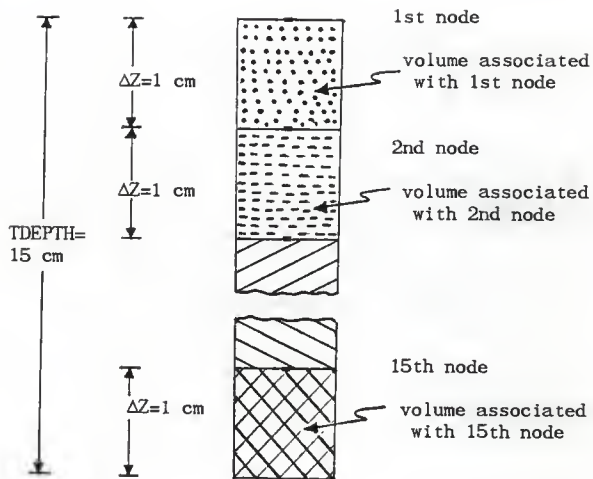


Figure 2-1. Schematic arrangement of nodes and soil depth increments associated with each node

The first term on the left-hand side of equation (1-60) contains ΔZ which is defined by:

$$\Delta Z = Z_{i+1} - Z_i$$

For the PC model, ΔZ is equal to the specific volume of a node, as is evident from Figure 2-1. For the Combined Model, ΔZ and specific volumes are unequal because of the chosen soil geometry. Therefore, replacement of ΔZ by the specific volume, in equation (1-60) is mathematically justifiable, in the case of the PC Model, but is not so in the case of the Combined Model. This reasoning forms the basis for the change in soil geometry made in the PC Model.

The boundary condition used at the soil surface is that there is no mass transfer to the soil surface from the air above the surface. This condition implies:

$$D_{i-1/2} = 0, i=1 \dots \dots \dots (2-6a)$$

A second boundary condition used in the application of equation (1-60) is that there is no diffusion of mass from the last node:

$$D_{i+1/2} = 0, i=M \dots \dots \dots (2-6b)$$

The convective transport term, $\bar{N}_i$, in equation (1-60) will now be examined. From Chapter 1, it may be recalled that the method used to compute $\bar{N}_i$ is different from the method outlined by Campbell (1985). In the development of the PC Model, an attempt was made to use the approach suggested by Campbell (1985) to incorporate convective mass transfer. However, this approach led to the prediction of unrealistic values for urea concentrations in soil solution. The probable cause of error in the method outlined by Campbell (1985) is that it is assumed that soil water fluxes for all nodes are either in the upward

direction or in the downward direction. In view of this probable shortcoming, the method developed, as part of this research, considers 27 theoretical possibilities for the calculations of $\bar{N}_i$ for each node. The method developed for this research yielded reliable results for the mass balances of the various chemical species.

Figure 2-2 depicts a general layout for the concentration of any chemical species and soil water flux for nodes $i-1$, i and $i+1$. The concentration of the species is the weighted average concentration for the new time step, $n+1$ and is given by equation (1-60). To compute $\bar{N}_i$ which is taken to be a source term in equation (1-60), the values of $\bar{C}_{i-1}$, $\bar{C}_i$ and $\bar{C}_{i+1}$ are needed as well as the values of soil water fluxes, $\bar{q}_{i-1}$, $\bar{q}_i$ and $\bar{q}_{i+1}$. It should be noted that while the C_i -values are all positive by definition, the $\bar{q}_i$ -values may be positive, negative or zero. A positive value of $\bar{q}_i$ implies downward soil water flux while a negative value of $\bar{q}_i$ means that the soil water flux is in the upward direction. A zero value for $\bar{q}_i$ simply means there is no water flux. The boundary conditions used in the computations of $\bar{N}_i$ are:

- (i) $\bar{q}_{i-1} = 0$, $i=1$
- (ii) $\bar{q}_i = 0$, $i=1$ (if $\bar{q}_i$ is negative)
- (iii) $\bar{q}_i = 0$, $i=M$

The first boundary condition means that there is no soil water flux from above the soil surface. The second condition is for the case when the computed soil water flux for the surface node is negative. The third boundary condition simply states that there is no soil water flux out of the last node.



$\bar{q}$ = weighted average soil water flux

$\bar{C}$ = weighted average concentration

Figure 2-2 Schematic arrangement of concentration and soil water flux associated with nodes.

Mathematically, there are 27 different possibilities for computing $\bar{N}_i$. As an example, consider the possibility that $\bar{q}_{i-1}$ is zero, $\bar{q}_i$ is positive and $\bar{q}_{i+1}$ is negative. For this case, $\bar{N}_i$ is given by:

$$\bar{N}_i = -\bar{q}_i \bar{C}_i - \bar{q}_{i+1} \bar{C}_{i+1} \dots \dots \dots (2-7)$$

A negative value of $\bar{q}_{i+1}$ implies that mass is transported into node i from node (i+1). Hence, in equation (2-7), a negative sign precedes the term $\bar{q}_{i+1} \bar{C}_{i+1}$ so that its value is positive. Similarly, a positive value of $\bar{q}_i$ means that mass is transported out of node i into node (i+1). Therefore, a negative sign precedes $\bar{q}_i \bar{C}_i$ in equation (2-7) so that its value is negative.

All of the 27 possibilities are considered for calculating $\bar{N}_i$ for each node. This procedure is adopted for all mass balances made for the various chemical species. In order to implement this change it was found necessary to add subroutine CONVEC to the model.

As pointed out earlier, in order to compute $\bar{N}_i$, the value of $\bar{q}_i$ and $\bar{C}_i$ are needed in subroutine CONVEC. The $\bar{C}_i$ values are obtained from mass balances of various chemical species. For example, the carbonate species mass balance permits computation of the weighted average concentration of bicarbonate ions (assigned the variable name AHCO3 in the model). Concentrations of other carbonate species are obtained from the computed value of AHCO3 using the carbonate system equilibria relations discussed in Chapter 1. In a similar way, the ammoniacal species mass balance gives the weighted average concentration of ammonium ions (assigned the variable name ANH4AQ in the model). Once ANH4AQ is known, the concentrations of the other

ammoniacal species are computed using equilibrium relations for the ammonia system discussed in Chapter 1. Mass balances for calcium ions, hydrogen ions and urea provide weighted average concentrations for these species. Next, all of these mass balances will be examined in detail. The computation of soil water flux values (q_i -values) will be discussed later.

In Chapter 1, it was pointed out that in order to implement the Newton-Raphson Method for the solution of the unknown concentrations, it was necessary to obtain the partial derivatives of the quantity F_i with respect to the unknown concentrations. In the PC Model, the relevant partial derivatives are defined by:

$$\begin{aligned} A(I) &= -FN * D(I) + J * JA(I) \\ B(I) &= CAP(I) + FN * [D(I+1) + D(I)] + J * JB(I) \\ C(I) &= -FN * D(I+1) + J * JC(I) \end{aligned}$$

In the equations given above, the value of J may vary for the different mass balances made. For example, J is equal to 4 for the N-balance, as discussed in Chapter 1. The other variables are defined as follows:

$$A(I) = \frac{\partial F_i}{\partial C_{i-1}^{n+1}}$$

$$B(I) = \frac{\partial F_i}{\partial C_i^{n+1}}$$

$$C(I) = \frac{\partial F_i}{\partial C_{i+1}^{n+1}}$$

$$FN = \eta$$

$$D(I) = D_{i-1}$$

$$D(I+1) = D_i$$

$$JA(I) = \frac{\partial \bar{N}_i}{\partial C_{i-1}^{n+1}}$$

$$JB(I) = \frac{\partial \bar{N}_i}{\partial C_i^{n+1}}$$

$$JC(I) = \frac{\partial \bar{N}_i}{\partial C_{i+1}^{n+1}}$$

The incorporation of $JA(I)$, $JB(I)$ and $JC(I)$ in the defining equations for $A(I)$, $B(I)$ and $C(I)$ represents a change made as part of the development of the PC Model. The need to incorporate $JA(I)$, $JB(I)$ and $JC(I)$ stems from the fact that in the PC Model, a convective flux term, $\bar{N}_i$, has been included in the mass balances for all chemical species. As explained earlier in this chapter, $\bar{N}_i$ is a function of the weighted average concentrations, $\bar{C}_{i-1}$, $\bar{C}_i$ and $\bar{C}_{i+1}$, which in turn are functions of the new concentrations, C_{i-1}^{n+1} , C_i^{n+1} and C_{i+1}^{n+1} , respectively. It follows that the partial derivatives of F_i with respect to the new concentrations must also include the partial derivatives of $\bar{N}_i$ with respect to the same new concentrations. The computation of $JA(I)$, $JB(I)$ and $JC(I)$ will be illustrated by the example given earlier in this chapter, for the computation of $\bar{N}_1$. If equation (2-7) is rewritten in terms of the new concentrations, the following equation is obtained:

$$-\bar{N}_1 = \bar{q}_1 C_1^{n+1} + (1 -)\bar{q}_1 C_1^n + \bar{q}_{i+1} C_{i+1}^{n+1} + (1 -)\bar{q}_{i+1} C_{i+1}^n \quad (2-8)$$

The required partial derivatives are obtained from equation (2-8) and are as follows:

$$JA(I) = 0$$

$$JB(I) = \bar{q}_1$$

$$JC(I) = \bar{q}_{i+1}$$

It should be noted that in equation (2-8), a negative sign was placed before $\bar{N}_1$. This was necessary because $\bar{N}_1$ is incorporated with a negative sign before it, in all mass balances except in the H^+ mass balance. For H^+ mass balance, the convective flux of OH^- is incorporated in the balance with a plus sign before it. This was necessary because the effect of the convective flux of OH^- on the H^+ mass balance will be opposite to that of the convective flux of H^+ . It follows that the quantity, $JA(I)$, computed for H^+ will be equal in magnitude but opposite in sign to the same quantity computed for OH^- . Similar statements apply to the quantities $JB(I)$ and $JC(I)$. Hence, for H^+ mass balance the following relations apply:

$$JA(I) \equiv 0$$

$$JB(I) \equiv 0$$

$$JC(I) \equiv 0$$

It must be emphasized that the expressions derived earlier for $JA(I)$, $JB(I)$ and $JC(I)$ pertain to the example where $\bar{N}_1$ was given by equation (2-7). Equation (2-7) is not a general equation but, simply, the applicable convective flux for the stipulated soil water fluxes in the example. As pointed out earlier, the applicable convective flux is

one of the 27 possible relations for convective flux that may apply to a given node. Hence, it should be concluded that only one of the 27 possible relations, each, for JA(I), JB(I) and JC(I) applies to a given node.

The changes made in the H^+ mass balance will now be examined. In the Combined Model, the mass balance for H^+ was represented by the following equation:

$$F(I) = CAP(I) * [NH(I) - H(I)] - D(I) * [AH(I+1) - AH(I)] \\ + D(I-1) * [AH(I) - AH(I-1)] + U(I) \dots \dots (2-9)$$

The variables in equation (2-9) are defined as follows:

$F(I)$ = value of the function for node I (should be a small number, ideally equal to zero).

$NH(I)$ = new concentration of H^+ for node I

$H(I)$ = old concentrations of H^+ for node I

$AH(I)$ = weighted average concentration of H^+ for node I

$$= FN * NH(I) + (1-FN) * H(I)$$

$D(I)$ = lumped diffusivity of H^+ and OH^- for node I

$U(I)$ = hydrolysis rate of urea for node I

$CAP(I)$ = capacity term for node I

$$= 0.4343 * MASS(I) / [SBC * AH(I) * DT] \dots \dots (2-10)$$

$$SBC = SBCMAX * EXP\{-0.0853 * ABS[(PH(I) - 7.0) ** 3]\} \dots (2-11)$$

In equation (2-9), the variables defined for nodes other than node I are defined in a similar way. For the surface node ($I=1$), the quantity ($CO2LOS - NH3LOS$) was added to the right-hand side of equation (2-9). Thus, it was assumed that for each mole of $CO_{2(g)}$ lost or $NH_{3(g)}$ volatilized, per square meter of soil per second, one mole of

H^+ was removed from or added to the soil solution, respectively.

Based upon the theory presented in Chapter 1, this assumption was found to be incorrect. Therefore, in the PC Model, H^+ mass balance is given by the following equation:

$$F(I) = CAP(I) * [NH(I) - H(I)] - D(I+1) * [AH(I+2)-AH(I)] + D(I) * [AH(I+1)-AH(I)] + HSINK(I) - JH(I) + JOH(I) \dots \dots (2-12)$$

In equation (2-12), the variable HSINK(I) is defined by equation (1-43). It should be noted that in equation (1-43), all of the variables are dimensioned variables. For the sake of algebraic simplicity, subscript I was omitted from the variables names in equation (1-43). Further, the second and fifth terms in equation (1-43) are assumed not to exist for soil nodes below the surface node (for $I > 1$). These two terms account for the effect on soil pH due to $CO_{2(g)}$ loss and $NH_{3(g)}$ loss and are, hence, included in the mass balance for the surface node only (for $I=1$). The variables JH(I) and JOH(I) account for the effect on soil pH due to the convective flux of H^+ and OH^- , respectively. A comparison of equations (2-9) and (2-12) reveals that the variables D(I) and D(I-1) in equation (2-9) have been replaced by D(I+1) and D(I), respectively, in equation (2-12). This change was prompted by considerations for the syntax of Microsoft FORTRAN 77. If D(I-1) was retained as a variable, a variable D(0) is implied for I equal to 1. Since a variable name D(0) is not acceptable to the syntax of Microsoft FORTRAN, this change was necessary. Similarly, variable names, AH(I-1), AH(I) and AH(I+1) in equation (2-9) have been replaced by AH(I), AH(I+1) and AH(I+2), respectively, in equation (2-12).

The term, CAP(I), in equation (2-12), is defined by:

$$\text{CAP(I)} = [\text{WA(I)} * \{1 + \text{P2(I)}\} + \{\text{BD(I)} * 1000 * 0.4343 / (\text{SBC} * \text{AH(I+1)})\}] \\ * \text{VOL(I)} / \text{DT} \quad \dots \dots \dots (2-13)$$

where:

$$\text{SBC} = \frac{1}{[8.7237 * 10^{-6} * \text{PH(I)} ** 2 - 1.27026 * 10^{-4} * \text{PH(I)} + 4.716029 * 10^{-4}]} \\ \dots \dots \dots (2-14)$$

A comparison of equations (2-10) and (2-13) reveals that two additional terms, WA(I) and WA(I)*P2(I), are included in equation (2-13). The first term is negligible while the second term is relatively small compared to the third term. For modeling purposes these two terms may be ignored. Thus, equation (2-13) may be simplified to:

$$\text{CAP(I)} = \frac{\text{VOL(I)} * \text{BD(I)} * 1000 * 0.4343}{\text{SBC} * \text{AH(I+1)} * \text{DT}} \quad \dots \dots \dots (2-15)$$

In equation (2-15) the product [VOL(I) * BD(I) * 1000] is equal to the quantity MASS(I) in equation (2-10). Hence, it may be concluded that equations (2-10) and (2-15) are identical in form. However, a major difference exists in the two equations owing to how the quantity SBC is defined for the two equations. An investigation of equation (2-11) revealed that a fundamental basis for the particular form of the equation does not exist. The equation was proposed in the Annual Report (1985). Through personal communication with Kissel (1987), it was learned that equation (2-11) was considered to be a generalized equation which may be used to determine the buffering capacity of any soil. However, a check on the values of SBC obtained from the equation revealed that these values were approximately 3-4 times larger than the values obtained graphically. The data used to determine the SBC

values graphically is given in the Annual Report (1985). The quantity SBC, which is the reciprocal of the soil buffering capacity (on a unit mass of soil basis), is the slope of the plot of soil pH versus OH^- added per unit mass of soil, for a given pH. To resolve this discrepancy in SBC values, the data for Haynie soil, given in the Annual Report (9185), was fitted to a polynomial by the least squares method. The polynomial used was of the form:

$$y = ax^3 + bx^2 + cx + d \dots \dots \dots (2-16)$$

where:

$$y = \text{kmol OH}^- \text{ per kg of soil}$$

$$x = \text{pH}$$

The least squares fit to data provided the following values for the constants:

$$a = 2.9079 \times 10^{-6}$$

$$b = -6.35131 \times 10^{-5}$$

$$c = 4.716029 \times 10^{-4}$$

$$d = -1.1762861 \times 10^{-3}$$

The derivative dy/dx , is given by:

$$\frac{dy}{dx} = 3(2.9079 \times 10^{-6}) x^2 - 2(6.35131 \times 10^{-5})x + 4.716029 \times 10^{-4}$$

or

$$\frac{d(\text{OH}^-)/\text{kg soil}}{d \text{ pH}} = 8.7237x \times 10^{-6} x^2 - 1.27026x \times 10^{-4} x + 4.716029x \times 10^{-4} \dots \dots \dots (2-17)$$

Since the quantity SBC is defined to be the reciprocal of the quantity on the left-hand side of equation (2-17), the defining equation for SBC is found to be given by equation (2-14). It should be noted that

equation (2-14) is applicable to Haynie soil, only, and is based on the data for Haynie soil given in the Annual Report (1985).

In the PC Model, the changes made in the computation of $\text{NH}_3(\text{g})$ loss and $\text{CO}_2(\text{g})$ loss will now be examined. In order to understand these changes, it will be necessary, first, to see how these losses are computed in the Combined Model. The $\text{CO}_2(\text{g})$ loss, in the Combined Model, was computed from the following equations:

$$\text{RAC} = \text{RA}$$

$$\text{IF } (\text{RAC} < 1000) \text{ RAC} = 1000$$

$$\text{CO2LOS} = \text{P10LOS} * [\text{AHC03}(1) - \text{CO2G}(0)] / (10 * \text{RAC}) \quad (2-18)$$

$$\text{RA} = \text{RAC}$$

where:

RA = resistance to mass transfer of water vapor from soil surface, s/m

$$\text{CO2LOS} = \text{CO}_2(\text{g}) \text{ loss, kmol}/(\text{m}^2)(\text{s})$$

$$\text{P10LOS} = \frac{\partial[\text{CO}_2(\text{g})]}{\partial[\text{HCO}_3^-]}, \text{ evaluated at soil surface, } \frac{\text{kmol}/\text{m}^3 \text{ soil air}}{\text{kmol}/\text{m}^3 \text{ soil sol}}$$

$$\text{AHC03}(1) = [\text{HCO}_3^-], \text{ evaluated at soil surface, kmol}/\text{m}^3 \text{ soil sol}$$

$$\text{CO2G}(0) = [\text{CO}_2(\text{g})] \text{ evaluated for the air above soil surface, kmol}/\text{m}^3 \text{ soil air}$$

$$\text{RAC} = \text{arbitrary resistance, s/m}$$

The denominator on the right-hand side of equation (2-18) represents the resistance to mass transfer of $\text{CO}_2(\text{g})$ from soil surface to the air, above.

The ammonia volatilization loss was computed from the following equation (in the Combined Model):

$$\text{NH3LOS} = \text{P4LOSS} * [\text{ANH4AQ}(1) - \text{NH3G}(0)]/\text{RA} \dots \dots \dots (2-19)$$

where:

$$\text{NH3LOS} = \text{NH}_{3(g)} \text{ loss, kmol}/(\text{m}^2)(\text{s})$$

$$\text{P4LOSS} = \frac{\partial[\text{NH}_{3(g)}]}{[\text{NH}_4^+]}, \text{ evaluated for soil surface, } \frac{\text{kmol}/\text{m}^3 \text{ soil air}}{\text{kmol}/\text{m}^3 \text{ soil sol}}$$

$$\text{ANH4AQ}(1) = [\text{NH}_4^+], \text{ evaluated for soil surface, kmol}/\text{m}^3 \text{ soil sol}$$

$$\text{NH3G}(0) = [\text{NH}_{3(g)}], \text{ evaluated for the air above the soil surface, kmol}/\text{m}^3 \text{ soil air}$$

Equation (2-19) suggests that the resistance to mass transfer of $\text{NH}_{3(g)}$ from the soil surface is taken to be equal to RA. However, if RA computed to a value less than 1,000 s/m, both RA and RAC were set equal to 1,000 s/m. For the meteorological data set used in this research, the value of RA computes in the range 40 - 1,000 s/m. For most of the time, however, the value of RA lies in the range 50 - 500 s/m. This means that for the Combined Model, both RA and RAC assumed the arbitrary mass transfer resistance of 1,000 s/m. The use of an unjustifiable basis for computation of ammonia volatilization loss was the reason why a change was made in the PC Model. Before examining the theoretical basis for the change, it might be of interest to note that Singh and Nye (1986) report a mean measured value of 133 dm/hr for the mass transfer coefficient of $\text{NH}_{3(g)}$, at 25°C, and for an air-flow rate of 2 dm³/hr. Since resistance to mass transfer is simply the reciprocal of the mass transfer coefficient, the measured value of Singh and Nye (1986) translates to a value of 271 s/m for the resistance to mass transfer of $\text{NH}_{3(g)}$. This value is in close agreement with the arithmetic mean of RA for the range 50 - 500 s/m.

The theoretical basis for computation of mass transfer resistances for both $\text{CO}_{2(g)}$ loss and $\text{NH}_{3(g)}$ loss will now be examined. For turbulent mass transfer across a gas-liquid interface, the "penetration theory", of Higbie ((Treybal, 1980; Hines and Maddox, 1985), postulates that small fluid elements, at the surface of a liquid phase, contact the gas phase for an average time after which they penetrate into the bulk of the liquid phase. Each element is then replaced by another element from the bulk liquid phase. This model is described as the unsteady-state diffusion of a solute into a liquid phase of infinite thickness. The theory predicts that the mass transfer coefficient is proportional to the square root of the diffusivity of the solute. Although the "penetration theory" is given for mass transfer of a solute from the gaseous phase to the liquid phase, it is conceptualized for this research that the theory is equally applicable to mass transfer from the liquid phase to the gaseous phase. It should be noted that the computation of the resistance to mass transfer of water vapor is based on the von Kármán analogy of turbulent mass transport and is briefly dealt with by McInnes (1985). For the purpose of correlating the mass transfer coefficients of ammonia, carbon dioxide and water vapor, it is assumed, in this research, that the "penetration theory" is adequate.

Application of the "penetration theory" leads to the following equations:

$$\frac{k_{g, \text{NH}_3}}{k_{g, \text{H}_2\text{O}}} = \left[\frac{D_{\text{NH}_3\text{-air}}}{D_{\text{H}_2\text{O-air}}} \right]^{0.5} \dots \dots \dots (2-20)$$

$$\frac{k_{g, \text{CO}_2}}{k_{g, \text{NH}_3}} = \left[\frac{D_{\text{CO}_2\text{-air}}}{D_{\text{NH}_3\text{-air}}} \right]^{0.5} \dots \dots \dots (2-21)$$

where:

k_{g, NH_3} , $k_{g, \text{H}_2\text{O}}$, k_{g, CO_2} are the gas film mass transfer coefficients for $\text{NH}_3(\text{g})$, water vapor and $\text{CO}_2(\text{g})$, respectively; $D_{\text{NH}_3\text{-air}}$, $D_{\text{H}_2\text{O-air}}$, $D_{\text{CO}_2\text{-air}}$ are the diffusivities of $\text{NH}_3(\text{g})$, water vapor and $\text{CO}_2(\text{g})$ in air, respectively. The required diffusivities may be obtained from the following semi-empirical equation proposed by Fuller (1966):

$$D_{AB} = \frac{1.0 \times 10^{-9} T^{1.75}}{P[(\Sigma v_A)^{1/3} + (\Sigma v_B)^{1/3}]^2} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} \dots \dots \dots (2-22)$$

where:

D_{AB} = diffusivity of solute A relative to solvent B, m^2/s

T = absolute temperature, K

P = total pressure, atm

Σv = diffusion volume, m^3/kmol

M = molecular weight, kg/kmol

The diffusion volumes, for $\text{NH}_3(\text{g})$, air, water vapor and $\text{CO}_2(\text{g})$, as given by Hines & Maddox (1985), are:

$$\Sigma v_{\text{NH}_3} = 14.9 \times 10^{-13} \text{ m}^3/\text{kmol}$$

$$\Sigma v_{\text{air}} = 20.1 \times 10^{-3} \text{ m}^3/\text{kmol}$$

$$\Sigma v_{\text{H}_2\text{O}} = 12.7 \times 10^{-3} \text{ m}^3/\text{kmol}$$

$$\Sigma v_{\text{CO}_2} = 26.9 \times 10^{-3} \text{ m}^3/\text{kmol}$$

The molecular weights of $\text{NH}_3(\text{g})$, air, water and $\text{CO}_2(\text{g})$ are taken to be 17, 28.8, 18 and 44 kg/kmol, respectively. Substitution of the diffusion volumes and molecular weights in equation (2-22) leads to the following equations:

$$k_{\text{g},\text{NH}_3} = 0.984 k_{\text{g},\text{H}_2\text{O}} \dots \dots \dots (2-23)$$

$$k_{\text{g},\text{CO}_2} = 0.802 k_{\text{g},\text{NH}_3} \dots \dots \dots (2-24)$$

From the two-resistance theory (Treybal, 1980), it follows that:

$$\frac{1}{K_{\text{g},\text{NH}_3}} = \frac{1}{k_{\text{g},\text{NH}_3}} + \frac{m_{\text{NH}_3}}{k_{\text{l},\text{NH}_3}} \dots \dots \dots (2-25)$$

$$\frac{1}{K_{\text{g},\text{CO}_2}} = \frac{1}{k_{\text{g},\text{CO}_2}} + \frac{m_{\text{CO}_2}}{k_{\text{l},\text{CO}_2}} \dots \dots \dots (2-26)$$

where:

K_{g,NH_3} and K_{g,CO_2} are the overall mass transfer coefficients for $\text{NH}_3(\text{g})$ and $\text{CO}_2(\text{g})$, based on the gas phase; m_{NH_3} and m_{CO_2} are the Henry's Law constants for the solubility of $\text{NH}_3(\text{g})$ and $\text{CO}_2(\text{g})$ in water, expressed as the ratio of the concentration in the gas phase to the concentration in the liquid phase; k_{l,NH_3} and k_{l,CO_2} are the liquid film coefficients for $\text{NH}_3(\text{g})$ and $\text{CO}_2(\text{g})$ respectively; k_{g,NH_3} , k_{g,CO_2} and $k_{\text{g},\text{H}_2\text{O}}$ are the gas-film coefficients for $\text{NH}_3(\text{g})$, $\text{CO}_2(\text{g})$ and water vapor, respectively.

Since $\text{NH}_3(\text{g})$ is a very soluble gas, m_{NH_3} is small. If it is further assumed that k_{g,NH_3} and k_{l,NH_3} are numerically equal, then, in equation (2-25), the quantity $(m_{\text{NH}_3}/k_{\text{l},\text{NH}_3})$ may be ignored and equation (2-25) simplifies to:

$$\frac{1}{K_{\text{g},\text{NH}_3}} = \frac{1}{k_{\text{g},\text{NH}_3}} \dots \dots \dots (2-27)$$

By the same reasoning, the following relation may be derived:

$$\frac{1}{k_{g,H_2O}} \approx \frac{1}{k_{g,H_2O}} \dots \dots \dots (2-28)$$

Taking reciprocals of each side of equation (2-23) gives:

$$\frac{1}{k_{g,NH_3}} = \frac{1.016}{k_{g,H_2O}} \dots \dots \dots (2-29)$$

From equations (2-27), (2-28) and (2-29) it follows that:

$$\frac{1}{K_{g,NH_3}} \approx \frac{1}{K_{g,H_2O}}$$

$$R_{NH_3} \approx R_{H_2O} \dots \dots \dots (2-30)$$

where R_{NH_3} and R_{H_2O} are the resistances to mass transfer for $NH_3(g)$ and water vapor, respectively. For the PC Model, the quantity R_{H_2O} is the quantity RA in equation (2-19). The quantity, RA is computed in the subroutine RESIST of the PC Model. As mentioned earlier, the computation of RA is based on the von Kármán analogy for turbulent mass transport. No attempt was made, as part of this research to investigate into the computation of RA. However, it was observed that at times, the computed values of RA increased by more than two orders of magnitude from one time step to the following time step. Such drastic changes occurred at an approximate RA-value of 1000 s/m. Hence, in the PC Model, the maximum value for the resistance to mass transfer of ammonia (R_{NH_3}) is limited to 1,000 s/m. It was also observed that rapid soil drying resulted in a very rapid decrease in the values of RA. Such rapid fluctuations in RA-values resulted in

instability in the model. Therefore, to smooth out the rapid fluctuations, a backward weighting factor was used to compute the present value of RNH3, as given by the following equation:

$$\text{RNH3} = 0.85 \text{ RNH3P} + 0.15 \text{ RA} \dots \dots \dots (2-31)$$

where:

RNH3P is the mass transfer resistance for $\text{NH}_{3(g)}$ for the previous time step.

The resistance to mass transfer for $\text{CO}_{2(g)}$ will now be estimated. From equation (2-25), the following relation may be written:

$$\omega_r = \frac{\text{Resistance to mass transfer in gas film}}{\text{Overall resistance to mass transfer}} = \frac{1/k_{g,\text{CO}_2}}{1/K_{g,\text{CO}_2}} \dots \dots (2-32)$$

Substitution of equations (2-23), (2-24), (2-27) and (2-28) in equation (2-32) yields:

$$\frac{1}{K_{g,\text{CO}_2}} = \frac{1.267}{\omega_r K_{g,\text{NH}_3}} \dots \dots \dots (2-33)$$

or

$$\text{RCO2} = \frac{1.267 \text{ RNH3}}{\omega_r} \dots \dots \dots (2-34)$$

The value of ω_r is reported in the literature (Hines & Maddox, 1985) to be 0.02. This means that 98% of the resistance to mass transfer of $\text{CO}_{2(g)}$ is in the liquid phase. In view of the fact that $\text{CO}_{2(g)}$ is a relatively insoluble gas, the reported literature value of ω_r does not seem to be unreasonable.

It is now possible to write the modified equations for the computation of $\text{NH}_{3(g)}$ loss and $\text{CO}_{2(g)}$ loss. The equations for the PC Model are:

$$\text{NH3LOS} = [\text{NH3G}(2) - \text{NH3G}(1)]/\text{RNH3} \dots\dots\dots(2-35)$$

$$\text{CO2LOS} = [\text{CO2G}(2) - \text{CO2G}(1)]/\text{RCO2} \dots\dots\dots(2-36)$$

$$\text{RCO2} = 1.267 \text{ RNH3}/\text{FRAC} \dots\dots\dots(2-37)$$

where:

$\text{NH3G}(2)$ and $\text{CO2G}(2)$ are the concentrations of $\text{NH}_3(\text{g})$ and $\text{CO}_2(\text{g})$ for the surface node, kmol/m^3 soil air;

$\text{NH3G}(1)$ and $\text{CO2G}(1)$ are the concentrations of $\text{NH}_3(\text{g})$ and $\text{CO}_2(\text{g})$ in the air above the soil surface, kmol/m^3 soil air;

RNH3 is as defined earlier and RCO2 is the resistance to mass transfer of $\text{CO}_2(\text{g})$ from soil surface to the air above, s/m ;

FRAC is the fraction of overall mass transfer resistance for $\text{CO}_2(\text{g})$ in the gas film (two resistance theory). A comparison of equation (2-18) with equation (2-35) and equation (2-19) with equation (2-36) reveals that a further difference exists for the computation of the respective losses. This difference lies in the fact that actual concentrations of $\text{NH}_3(\text{g})$ and $\text{CO}_2(\text{g})$ in the soil air of the surface are used in the PC Model.

In order to understand the basis for incorporating soil respiration in the PC Model, it is necessary to consider the effect of soil water content on urea hydrolysis rate. During periods of low surface moisture content (1-3% on a kg/kg basis), hydrolysis of urea in the surface 1 cm of soil was practically reduced to zero. The hydrolysis of urea in the lower soil layers was also diminished owing to the fact that prior to the first irrigation, only a small proportion of the urea diffused to the lower soil layers. The periods of diminished urea hydrolysis at the soil surface coincided with the

periods of low moisture levels at the soil surface. Loss of moisture from the soil surface is a mass transfer operation. In the PC Model the resistance to mass transfer for water vapor is R_A , defined earlier. Hence, for the time periods that soil moisture at the soil surface remained low, the computed values of R_A were relatively small (approximately in the range 50-100 s/m). Owing to the diminished urea hydrolysis rates under dry surface conditions, the production of HCO_3^- was also considerably reduced. Operation of the PC Model under such conditions led to instability owing to the rapid loss of $\text{CO}_{2(g)}$. The instability was probably due to the fact that diffusion of alkalinity (HCO_3^-) toward the soil surface could not keep pace with the rapid loss of $\text{CO}_{2(g)}$. As the instability progressed, the model computed negative $\text{CO}_{2(g)}$ loss.

At this stage of this research, a further development of the PC Model was implemented. The improvement was aimed to eliminate the instability in the model by including soil respiration in the equilibria and to incorporate its effect in mass balances for carbonate species and H^+ . An immediate outcome of this development was the elimination of instability from the model. The effect of soil respiration on H^+ mass balance has been discussed earlier. The changes made in the carbonate species mass balance resulted in the following equation:

$$\begin{aligned}
F(I) = & CAP(I) * [NHCO_3(I) - HCO_3(I)] - D(I+1) * [AHC03(I+2) \\
& - AHC03(I+1)] + D(I) * [AHC03(I+1) - AHC03(I)] - U(I) \\
& - RESPIR(I) + UCA(I) - JHC03(I) - JCO3(I) - JCO2AQ(I) \\
& \dots \dots \dots (2-38)
\end{aligned}$$

where:

$F(I)$ = right-hand side of equation (2-38) evaluated for new time step, $\text{kmol}/(\text{m}^2 \text{ soil})(\text{s})$;

$CAP(I)$ = capacity term for node i , $\text{m}^3 \text{ soil sol}/(\text{m}^2 \text{ soil})(\text{s})$;
 $NHCO_3(I), HCO_3(I) = HCO_3^-$ concentrations at the end of present and previous time steps respectively, for node i , $\text{kmol}/(\text{m}^3 \text{ soil})(\text{s})$;

$D(I), D(I+1), D(I+2)$ = lumped diffusivities of carbonate species for nodes $i-1, i$ and $i+1$, respectively, divided by the respective DZ -values, $\text{m}^3 \text{ soil sol}/(\text{m}^2 \text{ soil})(\text{s})$;

DZ = distance between nodes, m ;

$AHC03(I), AHC03(I+1), AHC03(I+2)$ = weighted average concentrations of HCO_3^- for nodes $i-1, i$ and $i+1$, respectively, $\text{kmol}/\text{m}^3 \text{ soil sol}$;

$U(I)$ = production rate of carbonate species for node i , for new time step, $\text{kmol}/(\text{m}^2 \text{ soil})(\text{s})$;

$RESPIR(I)$ = soil respiration flux for node i , for new time step, $\text{kmol}/(\text{m}^2 \text{ soil})(\text{s})$;

$UCA(I)$ = rate of precipitation or dissolution of $\text{CaCO}_3(\text{s})$ for node i , $\text{kmol}/(\text{m}^2 \text{ soil})(\text{s})$;

JHCO3(I), JCO3(I), JCO2AQ(I) = convective flux of HCO_3^- , CO_3^{2-}
and $\text{CO}_{2(\text{aq})}$ for node i, $\text{kmol}/(\text{m}^2 \text{ soil})(\text{s})$.

All of the variables, above, except RESPIR(I), have been quantitatively defined in Chapter 1 and earlier in Chapter 2. The variable RESPIR(I) is defined by:

$$\text{RESPIR}(I) = \text{SRESP} * \text{EXP}[-Z(I+1)/0.05] * \text{VOL}(I) \dots \dots \dots (2-39)$$

where:

SRESP = soil respiration rate at soil surface, $\text{kmol}/(\text{m}^3 \text{ soil})(\text{s})$;

Z(I+1) = distance from soil surface to node i, m;

VOL(I) = specific volume of node i, $\text{m}^3 \text{ soil}/\text{m}^2 \text{ soil}$.

The value of SRESP was taken to be $2.8 \times 10^{-8} \text{ kmol CO}_{2(\text{g})}/(\text{m}^3 \text{ soil})(\text{s})$. This is the mean measured rate reported by Singh & Nye (1986). The value agrees with the applicable range of values [1×10^{-8} - $1 \times 10^{-7} \text{ kmol}/(\text{m}^3 \text{ soil})(\text{s})$] given by Campbell (1985).

One of the changes made in the ammoniacal species mass balance is the inclusion of the convective fluxes, JNH4AQ(I) and JNH3AQ(I) for NH_4^+ and $\text{NH}_{3(\text{aq})}$, respectively. A second change made was in the computation of the adsorption of NH_4^+ . The value for the constant NK1 in the Freundlich equation, was averaged from the data presented by Singh and Nye (1986) and from the data given by Izaurralde (1985). The modified Freundlich equation which describes the adsorption of NH_4^+ is:

$$\text{NH4AD} = \text{NK1} * (\text{NH4AQ})^{\text{NK2}} \dots \dots \dots (2-40)$$

where:

NH4AD = NH_4^+ adsorbed, $\text{kmol}/\text{kg soil}$

NK1 = empirical constant equal to 1.9×10^{-3}

NK2 = empirical constant equal to 0.66

NH_4AQ = concentration of NH_4^+ , kmol/m^3 soil sol.

For a given time step, NH_4^+ adsorbed is computed from the following equation:

$$\text{ADS(I)} = \text{P6(I)} * [\text{NNH}_4\text{AQ(I)} - \text{NH}_4\text{AQ(I)}]$$

where:

$$\text{ADS(I)} = \text{NH}_4^+ \text{ adsorbed, kmol/kg soil}$$

$$\text{P6(I)} = \frac{\partial[\text{NH}_4^+(\text{ad})]}{\partial[\text{NH}_4^+]}, \frac{\text{kmol/kg soil}}{\text{kmol/m}^3 \text{ soil sol}}$$

$\text{NNH}_4\text{AQ(I)}, \text{NH}_4\text{AQ(I)}$ = NH_4^+ concentrations at the end of present and previous time step, kmol/m^3 soil sol

The changes made in the Ca^{2+} mass balance follow. In the computation for $\text{CaCO}_3(\text{s})$ precipitation or dissolution, the quantity, CHECKC was redefined to be the product of ACA(I+1) and ACO3(I+1) which are the weighted average concentrations of Ca^{2+} and CO_3^{2-} , respectively, for node i. Similarly, in the defining equations for the quantities G1 and C1, the weighted average concentrations of Ca^{2+} and CO_3^{2-} were used. The sign of the quantity, UCA(I) , which is a source/sink term in Ca^{2+} mass balance and C-balance, was changed so that it was defined as a positive quantity for $\text{CaCO}_3(\text{s})$ precipitation and as a negative quantity for the dissolution of $\text{CaCO}_3(\text{s})$. This change made it necessary to change the sign of UCA(I) in the two balances. The equation for the calculation of NCALC(I) was also modified as given below:

$$\text{NCALC(I)} = \text{CALC(I)} \pm [\text{DELTA}/\{\text{WA(I)} * \text{VOL(I)}\}] \dots \dots \dots (2-41)$$

where:

CALC(I), NCALC(I) = $\text{CaCO}_3(\text{s})$, concentrations at the end of previous and present time steps, respectively, for node i, kmol/m^3 soil sol;

DELTA = $\text{CaCO}_3(\text{s})$ precipitated or dissolved, kmol/m^2 soil;

WA(I) = soil water content for node i, m^3 soil sol/ m^3 soil;

VOL(I) = specific volume for node i, m^3 soil/ m^2 soil

The plus sign before the quantity in brackets is applicable for $\text{CaCO}_3(\text{s})$ precipitation and the minus sign for $\text{CaCO}_3(\text{s})$ dissolution.

In the Combined Model, NCALC(I) was calculated from:

$$\text{NCALC(I)} = \text{CALC(I)} \pm \text{DELTA} \dots \dots \dots (2-42)$$

Equation (2-41) is dimensionally consistent, the units being kmol/m^3 soil sol. The units of equation (2-42) are inconsistent and hence, the need for the change made in the PC Model. For the sake of dimensional consistency, the equation from the PC Model, given below, is also a modified equation:

$$\text{IF } [\text{DELTA}/\{\text{WA(I)} \times \text{VOL(I)}\}] .\text{GT. ACALC(I+1)}$$

$$\text{DELTA} = \text{ACALC(I+1)} \times \text{WA(I)} \times \text{VOL(I)} \dots \dots \dots (2-43)$$

where ACALC(I+1) is the weighted average concentration of $\text{CaCO}_3(\text{s})$ for node i and is defined by:

$$\text{ACALC(I+1)} = \text{FN} \times \text{NCALC(I)} + \text{GN} \times \text{CALC(I)}$$

FN = forward weighting factor

$$\text{GN} = (1 - \text{FN})$$

The corresponding equation in the Combined Model was:

$$\text{IF } [\text{DELTA} .\text{GT. CALC(I)}] \text{ DELTA} = \text{CALC(I)} \dots \dots \dots (2-44)$$

From the definitions of DELTA and CALC(I), it follows that equation (2-44) is dimensionally inconsistent. All of the changes given above affect the value of the UCA(I), referred to earlier, in this discussion. Hence these changes have an effect on both, the C-balance as well as the Ca^{2+} -balance. In addition, since $\text{CaCO}_{3(s)}$ precipitation or dissolution also influences the H^+ mass balance, it may be concluded that these same changes will also influence the H^+ mass balance, although, to a minor degree. The one general change made in all mass balances was the inclusion of convective flux. Thus in the Ca^{2+} mass balance, the convective flux of Ca^{2+} is incorporated.

The changes made in subroutine UREA will now be described. At the beginning of this chapter, it was pointed out that one of the accomplishment of this research was to correct the error that led to the prediction of negative urea hydrolysis. In the Combined Model, the urea hydrolyzed, expressed as a percentage of urea applied, was given by PERUH where:

$$\text{PERUH} = 100[1 - (\text{UNHYD}/\text{TOTALU})] \dots \dots \dots (2-45)$$

where:

$\text{UNHYD} = \text{unhydrolyzed urea, kmol/m}^2 \text{ soil}$

$\text{TOTALU} = \text{total urea applied, kmol/m}^2 \text{ soil}$

It should be clear from equation (2-43), that PERUH will be negative if UNHYD is greater than TOTALU. Certainly, UNHYD should never be greater than TOTALU. Thus, the error in the Combined Model was in the computation of UNHYD which was calculated from:

$$\text{UNHYD} = \text{UNHYD} + [\text{NUAQ(I)} * \text{WA} * \text{VOL(I)}] + \text{USOLID(I)}$$

where:

NUAQ(I) = urea concentration in solution at the end of a time step, for node i, kmol/m^3 soil sol

USOLID(I) = concentration of precipitated urea for node i, kmol/m^2 soil

The computation for UNHYD was executed in a DO loop in order to sum UNHYD for all the nodes. The variable UNHYD was set equal to zero after PERUH was calculated. Therefore, for the next time step, new values of UNHYD and PERUH were calculated based on the new values of NUAQ(I), WA(I) and USOLID(I). There appears to be no error in the procedure used to compute UNHYD. Therefore, the only source of error could be attributed to the computed values of NUAQ(I) and/or WA(I). The predicted values of WA(I), which represent soil water content, have been shown (McInnes, 1985) to agree with field-measured values. By process of elimination, it was concluded that the error was due to the incorrect computation of NUAQ(I).

In order to correct this error, the change implemented in the PC Model involved adjustment of urea concentrations. The adjustment was made as follows:

$$\text{UAQ(I)} = \text{NUAQ(I)} * \text{WAP(I)} / \text{WA(I)}$$

$$\text{AUAQ(I+1)} = \text{NUAQ(I)} (\text{WAP(I)} / \text{WA(I)})$$

where

UAW(I) = urea concentration at the beginning of present time step, for node i, kmol/m^3 soil sol;

AUAQ(I+1) = weighted average urea concentration for the present time step, for node i, kmol/m^3 soil sol;

NUAQ(I) = urea concentration at the end of previous time step, for node i, kmol/m^3 soil sol;

WAP(I) = weighted average soil water content for previous time step, for node i, m soil sol/m soil;

WA(I) = weighted average soil water content for present time step, for node i, m soil sol/m soil.

In the Combined Model, both, UAQ(I) and AUAQ(I+1) were simply set equal to NUAQ(I).

A second change made in the UREA subroutine was to make a direct computation for PERUH. This was accomplished by:

$$\text{PERUH} = 100(\text{HYD}/\text{TOTALU}) \quad \dots \dots \dots (2-45a)$$

where HYD is the urea hydrolyzed and is computed by summing the product of U(I) and DT for all the nodes. The variable U(I), which represents urea hydrolysis rate [$\text{kmol}/(\text{m}^2\text{soil})(\text{s})$], is computed in subroutine HYDROL. The quantity, DT, is simply the magnitude of the time step, taken to be 300 seconds.

The other change made in the UREA subroutine involved the incorporation of the convective flux term in the mass balance for urea. As mentioned at the beginning of this chapter, convective transport of urea allows it to move into the lower soil layers for an irrigation or a precipitation event.

Derivation of the Equation for Soil Water Flux

A significant accomplishment of this research was the incorporation of convective fluxes in the mass balances for the various chemical species. In order to include convective mass transfer in the PC Model, it was found necessary to compute soil water flux for each node. The mathematical basis for the soil water

transport equations used in the PC Model is given by McInnes (1985). Therefore, in this thesis, only the derivation of the general equation for computing soil water flux will be given.

Soil water flux, J_w , is given by (McInnes, 1985):

$$J_w = -K_{w,\psi} \left(\frac{\partial \psi}{\partial Z} \right) - K_{w,T} \left(\frac{\partial T}{\partial Z} \right) \dots \dots \dots (2-46)$$

where:

- J_w = soil water flux, $\text{kg}/(\text{m}^2)(\text{s})$
- $K_{w,\psi}$ = hydraulic conductivity with respect to water potential $(\text{kg})(\text{s})/\text{m}^3$;
- $K_{w,T}$ = hydraulic conductivity with respect to temperature, $\text{kg}/(\text{m})(\text{s})(\text{K})$;
- $\psi = (\psi_m + \psi_g)$, J/kg ;
- ψ_m = matric water potential, J/kg ;
- ψ_g = gravitational water potential, J/kg ;
- T = soil temperature, K

From the definition of ψ , it follows that:

$$\frac{\partial \psi}{\partial Z} = \frac{\partial \psi_m}{\partial Z} - g \dots \dots \dots (2-47)$$

where g = acceleration due to gravity, m/s^2

After substituting equation (2-47) in equation (2-46), the finite difference equivalent of equation (2-46) is written as:

$$J_{w,i} = - \frac{K_{w,\psi,i}}{Z_{i+1} - Z_i} \left[(\psi_{m,i+1} - \psi_{m,i}) - g(Z_{i+1} - Z_i) \right] \\ - \frac{K_{w,T,i}}{Z_{i+1} - Z_i} (T_{i+1} - T_i) \dots \dots \dots (2-48)$$

In order to obtain soil water flux as a volumetric flux, $\bar{q}_1$, the right-hand side of equation (2-48) is divided by the density of soil solution which is taken to be 1000 kg/m^3 . The equation in the PC Model corresponding to equation (2-48) is:

$$\begin{aligned} JW(I+1) = & KW(I+1) * \{ PA(I+2) - PA(I+1) - GR * [Z(I+2) - Z(I+1)] \} \\ & - KVT(I+1) * [TA(I+2) - TA(I+1)] \quad \dots \dots \dots (2-49) \end{aligned}$$

where:

$JW(I+1)$ = soil water flux for node i , $\text{m}^3 \text{ soil sol} / (\text{m}^2 \text{ soil})(\text{s})$.

It should be noted that division by the quantity, $1000 * [Z(I+2) - Z(I+1)]$, is incorporated in equation (2-49) for the definitions of both $KW(I+1)$ and $KVT(I+1)$.

The other notable change made in subroutine SOILTW was to compute the diffusivity of water vapor in soil by the equation recommended by Sallam (1984). As given in Chapter 1, the same change was made for the calculation of the diffusivities of $\text{CO}_{2(g)}$ and $\text{NH}_{3(g)}$. A further change involved the calculation of saturated hydraulic conductivity from the equation recommended by Campbell (1985):

$$K_{\text{sat}} = 4.0 \times 10^{-3} * \left[\left(\frac{1.3}{\rho_b} \right)^{1.3b} * \exp(-6.9 * X_c - 3.7 * X_s) \right] \dots \dots (2-50)$$

where:

K_{sat} = saturated hydraulic conductivity, $(\text{kg})(\text{s})/\text{m}^3$;

ρ_b = bulk density of soil, Mg/m^3

b = a constant obtained from soil water desorption curve, taken to be 3.2

X_c = mass fraction of clay in soil

X_s = mass fraction of silt in soil

In the PC Model, ρ_b was varied with depth according to the field data given by McInnes (1985). From equation (2-50), it follows that the values of K_{sat} will also vary with depth. Therefore, $KSAT(I)$, which represents K_{sat} in the model, was defined to be a dimensioned variable.

A further improvement made in the modeling of ammonia volatilization, as part of this research, was the addition of two subroutines, IVALUE and DVALUE. These subroutines permit verification of the calculations made for the C-balance, N-balance, Ca^{2+} -balance and H^+ -balance. Verification for the C-balance and N-balance was accomplished by computing the quantities CRECOV and NRECOV, respectively. The defining equations for the quantities, expressed as a percentage, are:

$$CRECOV = \frac{100 \times CBAL}{TOTALU + RESP} \dots \dots \dots (2-51)$$

$$NRECOV = \frac{100 \times NBAL}{2 \times TOTALU} \dots \dots \dots (2-52)$$

where:

CRECOV = C accounted for on a cumulative basis, %

NRECOV = N accounted for on a cumulative basis, %

TOTALU = urea applied, $kmol/(m^2 \text{ soil})$

RESP = C entering the soil system from soil respiration, on a cumulative basis, $kmol/m^2 \text{ soil}$

The variables CBAL and NBAL are defined by:

$$CBAL = UNHYD + CLOS + DCT \dots \dots \dots (2-53)$$

$$NBAL = 2 \times UNHYD + NLOS + DNT \dots \dots \dots (2-54)$$

where:

UNHYD = unhydrolyzed urea, $\text{kmol/m}^2 \text{soil}$

CLOS = cumulative loss of $\text{CO}_2(\text{g})$ from soil surface, $\text{kmol/m}^2 \text{soil}$

NLOS = cumulative loss of $\text{NH}_3(\text{g})$ from soil surface, $\text{kmol/m}^2 \text{soil}$

DCT = cumulative change in C, summed for all carbonate species, $\text{kmol/m}^2 \text{soil}$

DNT = cumulative change in N, summed for all ammoniacal species, $\text{kmol/m}^2 \text{soil}$

The Ca^{2+} and H^+ mass balance calculations were verified by computing the following quantities:

$$\text{CAACT} = \frac{100 \times [\text{CANEW} + \text{CLCNEW} + \text{CAADNU}]}{\text{CAINIT}} \dots \dots \dots (2-55)$$

$$\text{HACT} = \frac{100 \times [\text{HNEW} + \text{HADSNU} - \text{HGEN}]}{\text{HINIT}} \dots \dots \dots (2-56)$$

where:

CAACT = % of initial Ca^{2+} accounted for

HACT = % of initial H^+ accounted for

CANEW = Ca^{2+} in solution at any given time, $\text{kmol/m}^3 \text{soil}$

CLCNEW = Ca^{2+} as $\text{CaCO}_3(\text{s})$ at any given time, $\text{kmol/m}^3 \text{soil}$

CAADNU = Ca^{2+} in the adsorbed phase at any given, $\text{kmol/m}^3 \text{soil}$

HNEW = H^+ in solution at any given time, $\text{kmol/m}^3 \text{soil}$

HADSNU = H^+ in the adsorbed phase at any given time, $\text{kmol/m}^3 \text{soil}$

HGEN = cumulative amount of H^+ produced or consumed by chemical reaction, $\text{kmol/m}^3 \text{soil}$

CAINIT = total initial Ca^{2+} , in solution, in the adsorbed phase and as $\text{CaCO}_3(\text{s})$, $\text{kmol/m}^3 \text{soil}$

HINIT = total initial H^+ in solution and in the adsorbed phase, $\text{kmol/m}^3 \text{soil}$

In order to compute HINIT, it was found necessary to develop an equation relating H^+ concentration in solution to its concentration in the adsorbed phase. This relationship was obtained by integrating the right-hand side of equation (2-17). A negative sign was placed before the right-hand side of equation (2-17) in order to satisfy equation (1-63). The integrated form of the equation obtained was:

$$y = 2.38194 \times 10^{-7} (\ln x)^3 + 1.9792 \times 10^{-5} (\ln x)^2 + 2.04814 \times 10^{-4} \ln x + 2.1332 \times 10^{-3} \dots (2-57)$$

where:

y = concentration of H^+ in adsorbed phase, kmol/kg soil

x = concentration of H^+ in solution, kmol/m³ soil sol

The constant of integration is the last term on the right-hand side of equation (2-57). The constant was determined for the initial condition.

$$y = 0, x = 1 \times 10^{-14}$$

The initial condition implies that at pH 14, H^+ do not exist in the adsorbed phase. The initial H^+ concentration of pH 6.4 was therefore obtained from equation (2-57) by substituting into it the H^+ concentration corresponding to pH 6.4.

The changes made in the convergence criteria will now be described. In the Combined Model, convergence was assumed for the mass balances of N, C, Ca^{2+} , H^+ and urea when the following condition was met:

$$\left| \frac{\sum F_{i,j} - \sum F_{i,j-1}}{\sum F_{i,j}} \right| < 0.01 \dots (2-58)$$

where the quantity within the two vertical lines represents an absolute value. The subscripts j and $j-1$ denote the evaluation of the quantity ΣF_i for the present and previous iterations, respectively, for a given time step. The F_i -values are as defined by equation (1-67).

It was determined for this research that the condition given by equation (2-58) was met despite the fact that ΣF_{ij} was a relatively big number. It may be recalled from Chapter 1, that ideally, the F_i -values should all approach to zero. Thus, for this research, it was established that for the mass balances of C, N, Ca^{2+} and H^+ , the following convergence criteria are applicable.

$$\text{For } \text{H}^+ \text{ - balance: } F_{i,j} < 5.0 \times 10^{-18}$$

$$\text{For N - balance: } F_{i,j} < 5.0 \times 10^{-16}$$

$$\text{For C - balance: } F_{i,j} < 5.0 \times 10^{-14}$$

$$\text{For } \text{Ca}^{2+} \text{ - balance: } F_{i,j} < 5.0 \times 10^{-12}$$

The results obtained from the verification of mass balances (Table 7, Appendix C) suggest that the criteria given above are reasonable. For subroutine UREA and subroutine RESIST, the convergence criterion used in this research is of the same form as given by equation (2-58). However, a number 0.005 instead of 0.01 is used for convergence in subroutine RESIST. By using the number 0.005, accuracy of at least two significant figures is assured (Chapra and Canale, 1985).

As mentioned in Chapter 1, the Thomas Algorithm was used to compute the new concentrations for a time. In the PC Model, the Thomas Algorithm is represented by subroute SOLVE which also permits computation of the new temperature and new matric water potential for

the various soil nodes. In the Combined Model, mass balances for the chemical species as well as the water flux balance and the energy balance were made for all but the last node. In the PC Model, mass balances for the chemical species are made for all 15 soil nodes considered. This was made possible by defining one additional depth beyond the depth of the last node from the surface. This change was necessary in order to ensure verification of the mass balances. The water flux and energy balances, however, are made for all but the last node, as in the Combined Model. The only change made in the energy balance was that the temperature of the last node was set equal to the measured soil temperature for the 15-cm depth. This value was obtained from the meteorological data set.

Since subroutine SOLVE was used to compute the new values for all the balances, some new equations were added to subroutine SOLVE to check for the number of nodes. A further modification of subroutine SOLVE involved the computation of the variable DVAL. For the water flux and energy balances, the value of DVAL, in the first equation given below, was multiplied by a factor of 0.25. In the second equation, the value of F(I) was multiplied by 0.25. The equations, taken from the Combined Model, are:

$$DVAL = F(N)/B(N)$$

$$DVAL = F(I) - C(I)*DVAL$$

The mathematical implications of this change are beyond the scope of this research. The justification for this change, in general terms, is that it facilitates convergence by making the change in the value, for an iteration, smaller. It was found by experiment that without

this change, the computed new values for the water potential were grossly in error because the computed soil water content varied, for example, from 1% to 25% for a time step of 300 seconds. In the absence of irrigation or precipitation (rainfall), such abrupt changes in a time period of 300 seconds are impossible. It should be noted that no significant differences, in either the computed soil temperature or the computed water content, were observed for the two cases (with and without multiplication by 0.25) as long as the abrupt changes, mentioned above, did not occur. Such abrupt changes occurred during periods of rapid drying of soil at the surface.

The meteorological data set used in the PC Model consisted of the values of the key environmental factors that affect soil temperature and soil water content. The data set was collected by McInnes (1985) for the same period of time as the field study on ammonia volatilization (McInnes et al., 1986). The values in the data set were given at five-minute intervals, starting from 180:20 (Julian day: hour) to 195:12. For the PC Model, the data set was extrapolated to 195:20.

Prior to the initiation of this research, the data was stored on a tape in a PDP-11 computer format. As part of this research, the data set was transferred from the tape to the mainframe computer at Kansas State University. The format of the data was changed and subsequently the data set was downloaded to a PC. It was found that data for the time period, 184:17 to 185:9 was given at one hour intervals only. In order to interpolate values at 5-minute intervals, for this time period, short computer programs, were written. A further change made in the data set was to calculate values of vapor density

and to include them in the data set. The values of vapor density were calculated from measured values of dry and wet-bulb temperatures. The equation used to compute vapor density from wet and dry bulb-temperature values was recommended by Kanemasu (1987).

A final, major change implemented for this research involved restructuring the sequence of calculations. This change was prompted by the fact that three new subroutines were added in the development of the PC Model. A second reason for this change was that in the Combined Model, the UREA subroutine was linked in a sequence that permitted urea to have hydrolyzed at the time of application. A third reason for the change was out of considerations for reading of data from data files (Tables 9, 10, 11, Appendix C), writing data on the computer terminal (screen) and to an output file (Table 1, Appendix C). These reasons may be better understood in conjunction with a description of the sequence of calculations in the model. Hence, a description of the flow of calculations, in the PC Model follows.

MODEL FLOWS

As shown in Figure 2-3, the first step in the flow of calculations involves a definition of the equilibrium constants (K-values) and diffusion coefficients (D-values) of the various chemical species, as functions of temperature. In the second step, values for modeling and sensitivity parameters, are read from the data file, PARAM.DAT (Table 10, Appendix C). The parameter values are then written to an output file (Table 1, Appendix C). The values of the modeling parameter, TDEPTH and M, are used in equations (2-3) and (2-4) to

define the various nodal depths. A complete definition for the soil profile requires a definition for the soil surface depth (considered equal to zero) and the depth corresponding to a fictitious node above the soil surface (considered equal to zero). Once the soil profile is defined, the next step in the flow of calculations involves the definition of soil characteristics, such as sand content, silt content, bulk density and other characteristics described by McInnes (1985), and given in Table 11, Appendix C. Assumed initial values for soil temperature and water content (for all the nodes) are also read from this same data file. For the given soil characteristics and based on the assumed initial soil temperature and initial water content, the remaining soil properties such as nodal mass, total porosity, air-filled porosity, saturated hydraulic conductivity, saturated vapor density (of soil air), matric water potential and other soil properties are computed. At the same time, a soil respiration rate is also defined as given by equation (2-39).

The values of the various soil characteristics along with the values of the constant and variable soil properties are then, transferred from the main program to subroutine SOILTW with the help of COMMON statements. In subroutine SOILTW, the first statement that is executed is a READ statement. In Figure 2-3, the READ statement is shown separated from subroutine SOILTW in order to illustrate the fact that program execution is terminated when the end of the meteorological data set is encountered. The values, read from the meteorological data file WEATHER.DAT are for: Julian day, hour, minutes, wind speed, soil surface temperature, air temperature (at 1.6m above

soil surface), soil temperature at 6-cm depth, soil temperature at 15-cm depth, soil temperature at 30-cm depth, incident short wave radiation, reflected short wave radiation, vapor density of air, cloud cover (expressed as a fraction) and precipitation (rain or irrigation). A sample of meteorological data used in the model is given in Table 9, Appendix C. For this research, it was decided to write the results obtained from the model to an output file, every six hours, starting at 181:0. Meteorological data values, corresponding to the same time, are also written to the same output file.

The equations used for the computations made in subroutine SOILTW and subroutine RESIST are given by McInnes (1985) and are, therefore, not derived or explained in this thesis. In general, two interdependent balances, the energy balance and the water flux balance, are made for all but the last node. A no-flow boundary condition is used for the last node. The water flux balance permits computation of new values for the matric water potential for a given time step. The weighted-average (weighted in time in the same way as concentrations) water potential values are used to compute the weighted-average soil water content for all the nodes. The energy balance directly provides new values of soil temperature for all the nodes. The weighted-average soil temperature values are then computed from the new temperatures by using a forward weighting factor as was done to calculate the weighted-average concentrations. The weighted-average values of soil water content and temperature are used to compute, the

air-filled porosity of soil, the saturated vapor density of soil air, the diffusivity of water vapor and water activity.

Figure 2-3 shows that the flow of calculations transfer from subroutine SOILTW to subroutines SOLVE and RESIST. As mentioned earlier, subroutine SOLVE is simply the Thomas Algorithm which, in this case, is used to compute new values for soil water potential and temperature, until convergence is obtained. In subroutine RESIST, resistances to mass transfer of water vapor (from or to soil surface) and the resistance to heat transfer (from or to soil surface) are computed. The computation for the resistances is based on the soil surface temperature calculated from the energy balance in subroutine SOILTW. The von Kármán analogy, for turbulent heat, mass and momentum transfer, is used in subroutines RESIST to compute the resistances. The relevant theory is discussed by McInnes (1985) and is therefore omitted from this thesis.

After convergence is obtained in subroutine SOILTW, the flow of calculations passes back to the main program. In the main program, as shown in Figure 2-3, the subsequent flow of calculations depends on the value of a variable MFLAG (denoted by FLAG in Figure 2-3). The value of MFLAG is, initially, set equal to 1. This allows initialization of concentrations for the various chemical species. The value of MFLAG is then set equal to 2, so that, subsequently, the initialization step is by passed. After the initialization step, the initial concentrations are stored in subroutine IVALUE. In the next step, the initial concentrations as well as the initial water content and temperature (for all nodes) are written to an output file by calling

subroutine OUTPUT. In the next step (not shown in Figure 2-3), key information and results are printed on the terminal. The following values are printed in the same order as given: Julian day, hour of day, minutes past the hour, soil surface pH, surface soil water content, surface soil temperature, percent urea hydrolyzed, percent ammonia-N loss, percent N accounted for (time step basis), percent C accounted for (time step basis), percent N-accounted (cumulative basis), percent C accounted (cumulative basis) and urea hydrolyzed from soil surface (expressed as a percentage of total hydrolyzed for the time step). The values of variable soil properties are then updated in subroutine UPDATE. This ensures that the calculated new values are the initial values for the next time step. Finally a check for end of meteorological data file is made. In the event, the end has not been reached, the flow of calculations once again transfers to subroutine SOILTW. The major calculation steps in subroutine SOILTW have been described earlier. It was assumed, earlier, that convergence is obtained in subroutine SOILTW. If, however, convergence is not obtained, the calculations continue after the errors in the energy balance and in the water flux balance are printed on the terminal and written to the output file. This allows detection of unusually big errors which are likely to affect other results of the model.

Once again, a check is made for the value of MFLAG. Since its value for the first time step was set equal to 2, calculations for initialization of concentrations are bypassed. At this stage, a check is made to see whether more than 99.99% urea has been hydrolyzed or not. In the event that urea hydrolyzed is greater than 99.99%, the

calculations in subroutine UREA are bypassed. For the case that hydrolyzed urea is less than 99.99%, the major calculation steps follow. First of all, the total applied urea is set equal to urea existing as a solid at the soil surface:

$$USOLID(1) = TOTALU, \text{ kmol/m}^2 \text{ soil.}$$

Subsequently, a check is made to determine whether or not the calculations in subroutine UREA are for the first time step. In case the calculations are for the first time step, urea concentration is not updated which means that the initial concentration for the present time step is not set equal to the new concentration of the previous time step. For the second and subsequent time steps, urea concentration is updated as well as adjusted for water content as described earlier in the section pertaining to the changes made for the PC Model. In the next step of calculations, urea concentration, at the beginning of a time step of calculations, is adjusted with respect to its solubility (at the weighted average temperature for the time step) and with respect to the urea present in the solid phase. If urea concentration is greater than its solubility, its concentration is set equal to its solubility. The change in urea concentration, converted to a square meter of soil surface basis, is added to the urea present in the solid phase. It should be noted that dimensionally consistent units are used in equations when a change in concentration for the solution phase is added to the urea present in the solid phase and vice versa. In the event, urea concentration is less than its solubility, and, also, if urea present in the solid phase is greater than

this difference (in consistent units), then urea concentration in solution is set equal to its solubility and urea present in the solid phase is proportionately decreased (in consistent units). If, however, urea concentration in solution is less than the solubility, and urea in the solid phase is less than the difference between solubility and the solution concentration (in consistent units), then the solution concentration is increased by an amount equal to urea present in the solid phase (in consistent units), while, the solid phase content of urea is set equal to zero.

After the adjustment of initial urea concentration is completed, the new and weighted average concentrations of urea (calculated from mass balance) are set equal to the initial concentration. The next step of calculations involves the computation for the diffusivity of urea from equations (1-46) and (1-61). At this stage, the flow of calculations transfers to subroutine HYDROL where rate of urea hydrolysis ($\text{kmol}/(\text{m}^2\text{soil})(\text{s})$) is computed for each node. The form of equation used to compute urea hydrolysis rate is given by equation (1-4). For this equation, the maximum rate of hydrolysis, VMAX, is computed from the following equations:

$$M310 = (4.259 \times 10^{-9} * \text{OCARB} + 1.4079 \times 10^{-9})/\text{MWU} \quad \dots (2-58)$$

$$\text{VM} = M310/\text{EXP} [-\text{AE}/(\text{R}*310.0)] \quad \dots (2-59)$$

$$\text{VMAX} = \text{VM} * \text{EXP} [-\text{AE}/(\text{R}*T)] \quad \dots (2-60)$$

where:

M310 = urea hydrolysis rate at 310K, $\text{kmol}/(\text{kg soil})(\text{s})$

OCARB = organic carbon content of soil, %

MWU = molecular weight of urea , kg/kmol

VM = empirical constant, kmol/(kg soil)(s)

AE = Arhenius Constant, J/mol

R = gas constant, J/(mol)(K)

VMAX = maximum rate of urea hydrolysis at T,K,
kmol/kg soil)(s)

It should be noted that in the Combined Model, the value of AE was taken to be 4.1×10^4 J/mol. The recent, unpublished data of Moyo (1988) suggests that a value of AE equal to 5.4×10^4 J/mol gives a better prediction for the effect of temperature on urea hydrolysis. Accordingly, in the PC Model, the value of AE is taken to be 5.4×10^4 J/mol. Equation (1-4) gives the urea hydrolysis rate for a unit mass of soil. When this rate is multiplied by the mass associated with each node ($\text{kg soil/m}^2 \text{ soil}$), urea hydrolysis rate, $U(I)$, is obtained in units of flux [$\text{kmol}/(\text{m}^2 \text{ soil})(\text{s})$]. The hydrolysis rate, in flux units, is the sink term in urea mass balance.

Additionally for the urea mass balance, the convective flux term is needed. This is computed (for all the nodes) in subroutine CONVEC. It may be recalled that subroutine CONVEC represents the development work done for this research.

Calculations for the urea mass balance, which follows next in the sequence, have been described, in some detail, in Chapter 1. It should be noted, here, that the partial derivatives to be evaluated, in order to apply the Newton-Raphson Method, are given in the model by the variables $A(I)$, $B(I)$ and $C(I)$. A new value for urea concentration is then computed in subroutine SOLVE. The entire process is repeated

until convergence is obtained. The convergence criterion for urea mass balance was given earlier in this chapter. If convergence is not obtained, an error in the mass balance is written to the output file as well as printed on the terminal.

The value of urea hydrolysis rate is transferred to the main program. The mass balances made in the main program are for the carbonate species, ammoniacal species, Ca^{2+} and H^+ . These balances have been discussed in detail in Chapter 1. Therefore, only the flow of calculations is now given. For each mass balance, computations made in subroutines CONVEC and SOLVE are needed. For the C-balance, subroutine CONVEC is required to compute convective fluxes for HCO_3^- , $\text{CO}_{2(\text{aq})}$ and CO_3^{2-} . For the N-balance, convective fluxes of NH_4^+ and $\text{NH}_3(\text{aq})$ are required. For the Ca^{2+} -balance, subroutine CONVEC computes the convective flux for Ca^{2+} . For the H^+ - balance, convective fluxes for H^+ and OH^- are computed. In subroutine SOLVE, new concentration for HCO_3^- , NH_4^+ , Ca^{2+} and H^+ are computed. The weighted average concentrations of the four chemical species are used to compute the weighted average concentrations of all other species. The mass balances are made in the sequence: C-balance, N-balance, Ca^{2+} -balance and H^+ -balance. If any of these balances converge, the value of FLAG is increased by 1. The value of FLAG was set equal to zero prior to proceeding with the mass balance step. Also, at the same time, the value of the number of iterations made was set equal to zero. All four mass balances are required to converge simultaneously (during the same iteration) in order to obtain overall convergence for the main program. If any one of the four balances do not converge, then the

value of FLAG is set to zero and the number of iterations are increased by 1. A maximum of 15 iterations was considered to be a reasonable number to allow all four balances to converge simultaneously. Overall convergence is obtained when the value of FLAG becomes equal to 4*M. If overall convergence is not attained, the errors for each mass balance are printed on the terminal. Additionally, if convergence is obtained, then too, the value of the quantity ΣF_{ij} for each mass balance is printed on the terminal along with the total number of iterations required for convergence.

The values of all concentrations are then updated which means that the new values for the present time step become the starting values for the next time step. The flow of calculations then passes on to subroutine DVALUE where a check for the mass balance calculations is made for the four balances, as described earlier. The values stored earlier, in subroutine IVALUE, are used in these mass balance checks. Next in sequence is subroutine IVALUE where all updated concentrations are stored. As mentioned earlier, these concentrations are the initial values for the subsequent time step and are, therefore, required in the computations for the mass balance checks for the subsequent time step.

In the next step of the model flow, the concentrations of NH_4^+ , HCO_3^- , $\text{NH}_3(\text{g})$, $\text{CO}_2(\text{g})$, Ca^{2+} , $\text{NH}_4^+(\text{ad})$, and urea along with the values of soil water content and soil temperature are written to the output file. It should be noted that these values are written for all the nodes considered (15 for the PC Model). The variable soil properties are then updated in subroutine UPDATE as was done for the initial

time. Finally, a check is made to determine whether end of meteorological data file has been reached or not. The entire flows of the model described until now are repeated until end of data file is reached. This is determined by checking the value of the logical variable FCLOSE. The value of FCLOSE was at first set equal to FALSE. When end of data file is reached, the value of FCLOSE is set equal to TRUE.

The description of model flows is now finished. In Chapter 3, model results will be examined and interpreted in the light of field data reported by McInnes et al. (1986). Results of sensitivity analysis of the model, conclusions from this research and recommendations for further research on modeling ammonia volatilization are also given in Chapter 3.

CHAPTER 3

RESULTS, CONCLUSIONS AND RECOMMENDATIONS

In this chapter, modeled results are presented, interpreted and compared with field results reported by McInnes et al. (1986). A brief discussion of the results obtained from a preliminary sensitivity analysis of the PC Model is also given in this chapter. Finally, conclusions drawn from this research and recommendations for future research directed toward modeling ammonia volatilization are given.

Figure 3-1 illustrates the modeled urea hydrolysis with time. The data used to develop Figure 3-1 are given in Table 2, Appendix C. Figure 3-2 is a reproduction of the results for the field study on ammonia volatilization from surface application of urea to Haynie soil (Study 3, McInnes et al., 1986). It should be noted that in Figure 3-2, soil water content and soil surface temperature plots were developed from modeled results reported by McInnes (1985).

From Figure 3-1, the predicted amount of urea hydrolyzed for the same duration as the field study is approximately 100%. A corresponding figure for the field study is not available. Figure 3-2, shows that the last measurement for the amount of urea hydrolyzed was made on 193:20 (Julian day: hour). From Figure 3-2, the amount of urea hydrolyzed on 193:20 is approximately 90%. In comparison, the predicted amount of urea hydrolyzed at the same time is estimated, from Figure 3-1, to be 94.4%.

The close agreement between modeled and measured amounts of urea hydrolyzed on 193:20 is in striking contrast with the disagreement

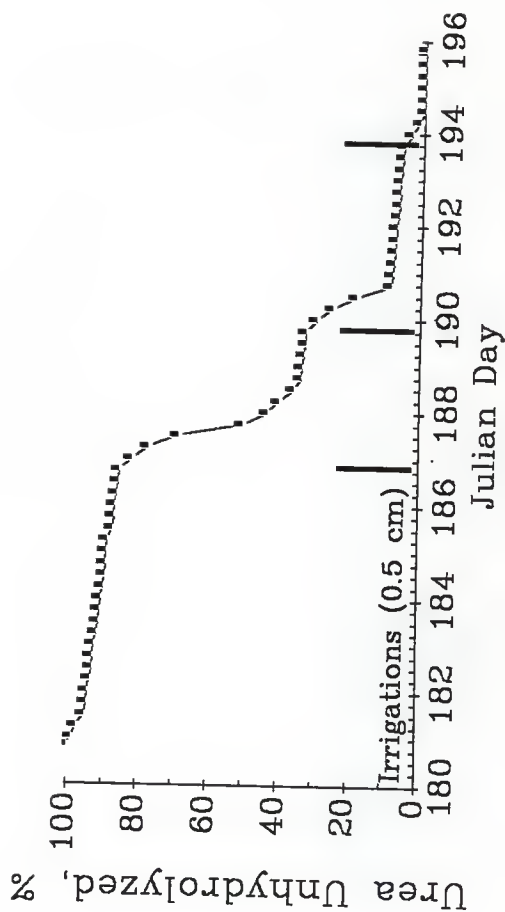


Figure 3-1. Modeled urea hydrolysis rate

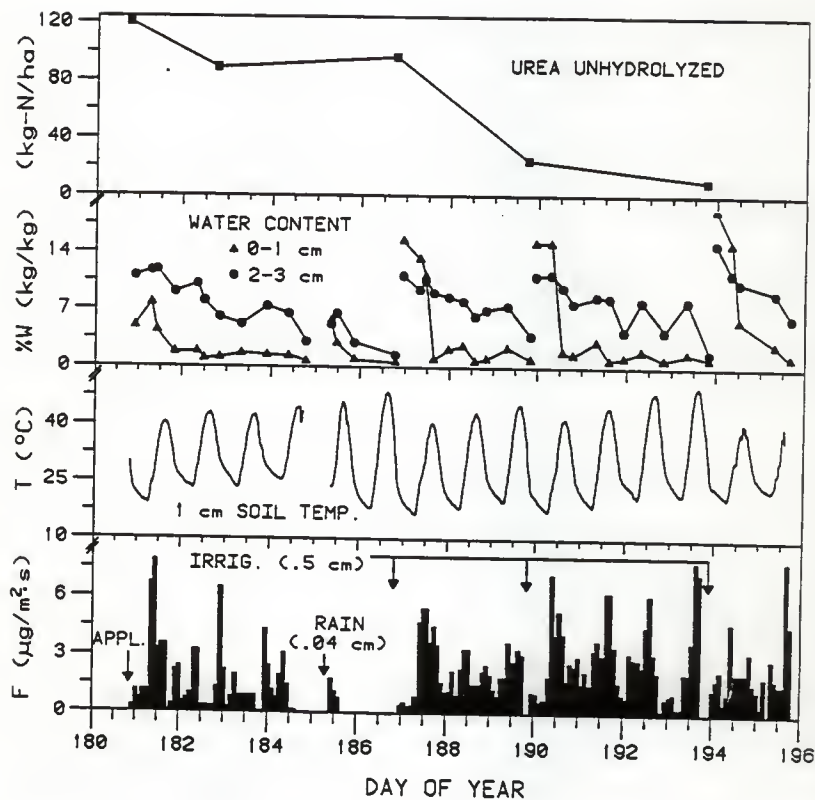


Figure 3-2. Urea hydrolysis, surface water content, surface temperature, and ammonia volatilization rate for study 3 (McInnes et. al., 1986).

between modeled and measured values on 182:20. From Figure 3-1 and 3-2, the modeled and measured amounts of urea hydrolyzed on 182:20 are estimated to be 7.2% and 25%, respectively. A closer examination of Figure 3-2, reveals a possible cause for the disagreement between modeled and measured values. Figure 3-2 shows that, the measured amount of urea hydrolyzed on 186:20 is, approximately, 18.5%. Since a decrease in the measured amount of urea hydrolyzed is indicated for the time period between 182:20 to 186:20, it is concluded that the measured amounts of urea hydrolyzed on 182:20 or on 186:20 or at both times, are apparently, in error. McInnes et al. (1986) do not account for the negative hydrolysis indicated by their data for this time period. On the other hand, they observe that "a considerable amount of urea was hydrolyzed during the first 2 days". Since the measured value for hydrolyzed urea on 182:20 is questionable, an appropriate explanation for the discrepancy between modeled and field results cannot be given.

From Figure 3-1, the modeled amount of urea hydrolyzed on 186:20 is approximately, 14.3%. Although the modeled amount is less than the corresponding measured value (18.5%), the difference between the modeled and measured values is considerably less than it is for 182:20. On 189:20 (time of second irrigation), the modeled and measured values for urea hydrolyzed are 67.3% and 77%, respectively.

The modeled urea hydrolysis rate is consistently less than the measured rate, although the difference between the two is considerably smaller toward the end of the time period of the field study. The slower rate predicted by the model may be due to the omission of mass

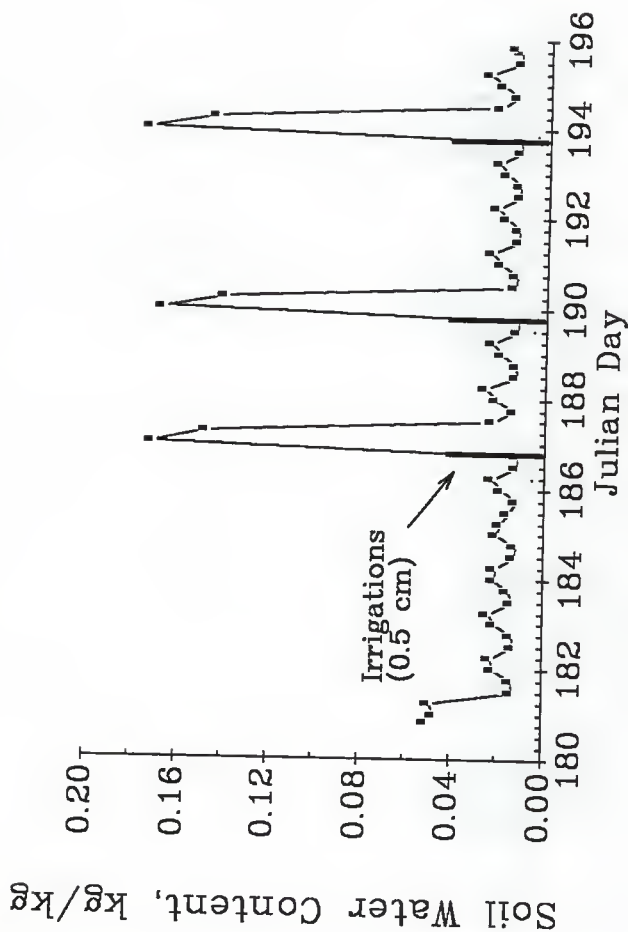


Figure 3-3. Modeled surface (0-1 cm depth increment) soil water content

transfer by dispersion in the model. According to Bresler (1973), mass transfer by dispersion is important during periods of infiltration (downward flow of soil water) while, during periods of redistribution and evaporation, mass transfer by diffusion is more important. During periods of redistribution and evaporation, the soil water content at the surface is expected to be low.

The surface (0-1 cm) soil water content remained at 1 to 3% during most of the field study. The surface (0-1 cm) soil water content based on the modeled results for this research is given in Figure 3-3. Data for Figure 3-3 are given in Table 8, Appendix C. It is observed, from Figure 3-3, that the surface soil water content remained in the 1-3% levels for most of the time during the simulated time period of the study. The rapid drying of the soil surface, after each of the three major irrigation events, suggests that periods of redistribution and evaporation of soil water dominated over the periods of infiltration. From the observations of Bresler (1973), given above, it follows that for a major portion of the simulated time period, the error in modeled results should be small because mass transfer by dispersion is unimportant. Therefore, the modeled results should, theoretically, be reliable for the periods of redistribution and evaporation of soil water.

During periods of infiltration, however, the model is expected to predict a slower urea hydrolysis rate than would be predicted if mass transfer by dispersion were included in the model. The last statement follows from the fact that solute transport by convection, diffusion and dispersion, together, is faster than the rate of

transport by convection and diffusion alone. Thus, if mass transfer by dispersion were to be included in the model, urea is expected to be transported, in significant amounts, to depths greater than those predicted by the present model. This in turn, should lead to an increased hydrolysis rate resulting from an increased urease activity at greater soil depths. It should be noted that the present model accounts for an increase in urease activity due to an increase in soil water content. The increase is accounted for by incorporating a water potential factor, $PEFF$, in equation (1-4).

In order to test the hypothesis that the slower hydrolysis rate predicted by the model is due to the omission of the dispersion term, it is necessary to examine field observations and data in more detail. McInnes et al. (1986) observed that after the first irrigation event on 186:20, "water content measurements showed that the irrigation water moved at least into the 4-5 cm depth increment". They go on to state that "it is likely that the urea was dispersed throughout the surface 5 cm, but a significant portion may have been in the 3-4 cm and 4-5 cm depths." The modeled results for this research will now be examined with reference to the observations and statements made by McInnes et al. (1986).

Figure 3-4 shows the predicted amounts of urea present at various soil depths on 186:18 (2 hours prior to the first irrigation) and on 187:18 (22 hours after the first irrigation). From Figure 3-4 and Table 3, it is observed that on 186:18, the 0 to 1 cm depth increment contains, approximately, 100% of total unhydrolyzed urea. However, on 187:18, significant amounts of urea are present down to the 3 - 4 cm

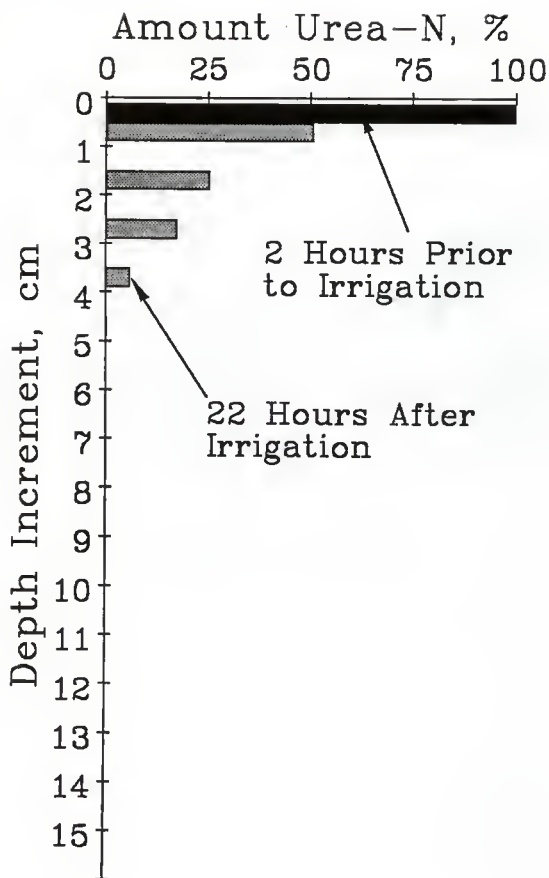


Figure 3-4. Effect of first irrigation (on 186:20) on the distribution of urea.

depth increment, but an insignificant amount is predicted in the 4 - 5 cm depth increment. It is further shown in Table 3, that the soil water content (denoted by WA in Table 3) in the 4 - 5 cm depth increment increased from, approximately, 11.7% (on a volume basis) to 13.2% during this time period. In the 5 - 6 cm depth increment, a negligible change in the soil water content occurred for the same time period.

The predicted results for infiltration of soil water are in general agreement with the field observations of McInnes et al. (1986), given earlier. However, the modeled data for the amount of urea present do not completely agree with the statement that "a significant portion may have been in the 3-4 cm and 4-5 cm depths". It therefore, follows that if, indeed, urea was transported in significant amounts to the 4-5 cm depth, the hypothesis for the slower hydrolysis rate predicted by the model should be correct. Hence, it is concluded that a possible cause for the slower hydrolysis rate predicted by the model is the omission of dispersion from the mechanism of mass transfer used in the model.

The modeled results for urea hydrolysis rate have a significant bearing on the modeled results for ammonia volatilization loss. From the theory, discussed in Chapter 1, it follows that if applied urea did not hydrolyze, ammonia loss would not occur. However, it should be understood that the mechanism of ammonia volatilization is complicated. It is, therefore, incorrect and oversimplistic to assume a mathematical relationship of direct proportionality between the rate of ammonia volatilization and the rate of urea hydrolysis.

The reported ammonia volatilization loss for the field study (McInnes et al., 1986) is 17% of the urea-N applied. In comparison, the modeled ammonia volatilization loss (Figure 3-5) was 16.3% (Table 1, Appendix C). Data for Figure 3-5, are given in Table 2, Appendix C. From Figure 3-5, the urea-N loss, on 186:20, is estimated to be 3%. The field loss at the corresponding time is reported to be 4%. Additional field data pertaining to the loss are presented as a bar graph of ammonia-N flux which is shown as part of Figure 3-2.

In an attempt to further compare modeled urea-N loss results with field results, Figure 3-6 was developed from the modeled data given in Table 2, Appendix C. McInnes et al. (1986) report "losses as high as $5.5 \mu\text{g} (\text{m}^2\text{s})^{-1}$ " on the day following the first irrigation (day 187). From Figure 3-6, it is observed that the peak modeled ammonia-N flux on the day after the first irrigation is $5.4 \mu\text{g}/(\text{m}^2)(\text{s})$. McInnes et al. (1986) further report peak rates of loss for day 192 and day 193. In comparison, the modeled results indicate that although relatively high losses occurred on days 192 and 193, peak rates of loss, occurred on days 190 and 191. From the data of Table 2, ammonia-N loss for days 190 and 191 is 3.7% while for days 192 and 193 the loss is 2.9%. Although corresponding values for the field study are not available, it appears from Figure 3-2 that the loss for days 190 and 191 is about equal to the loss for days 192 and 193. The higher modeled loss for days 190 and 191 is due, in part, to the faster urea hydrolysis rate during this period. From the data in Table 2, the amount of urea hydrolyzed on days 190 and 191 is computed to be about 22.3%. For days 192 and 193, the computed urea hydrolyzed is only

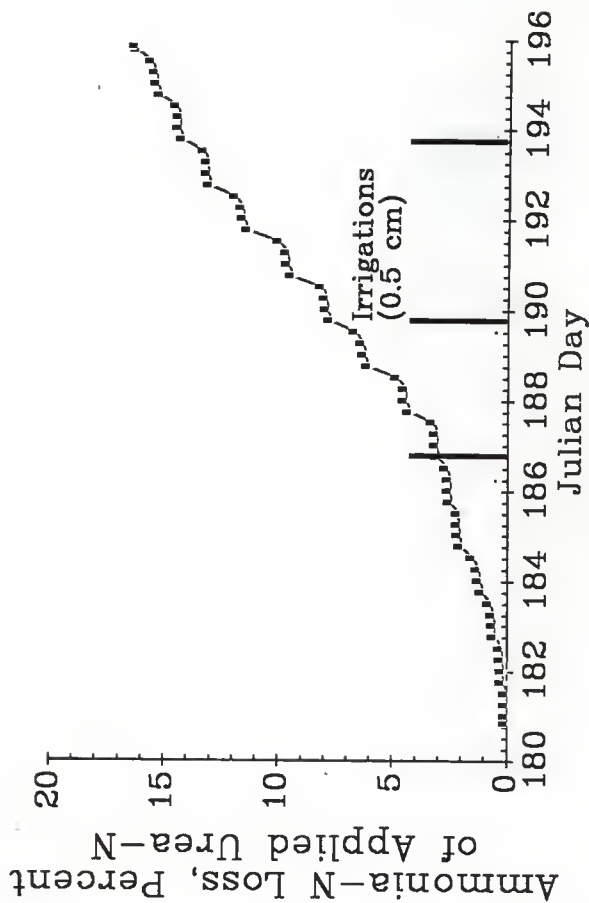


Figure 3-5. Modeled ammonia volatilization loss.

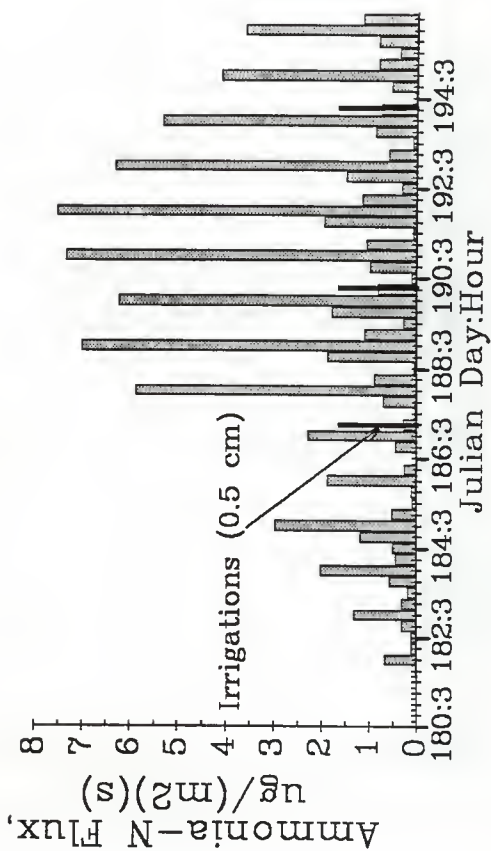


Figure 3-6. Modeled ammonia-N flux from soil surface.

3.8% suggesting that the urea-N loss for the period should also be relatively less. While the modeled results show that relatively less ammonia-N loss did occur on days 192 and 193 compared to the loss for days 190 and 191, field results suggest that the losses for the two time periods are about the same. Hence, there may be some disagreement between modeled and field results for urea-N losses during this period.

A comparison of Figures 3-2 and 3-6, for the time period between 180:20 and 186:20, indicates a discrepancy in the magnitude of peak fluxes. In view of the disagreement between the modeled and measured urea hydrolysis rate for the 2-day period after application of urea, the discrepancy in the magnitude of urea-N flux is not surprising.

Since tabulated data used to develop Figure 3-2 were not available, it is not possible to make any further detailed comparisons between modeled and field results. Estimation of data from Figure 3-2 is likely to introduce errors which in turn may be a cause for drawing incorrect conclusions.

A final observation made by McInnes et al. (1986) pertains to the amount of NH_4^+ -N in soil at the time the last measurement for urea hydrolysis was made. The analysis of soil samples showed that "there was almost an equal distribution in the surface 4 cm and a considerable amount in the 4-10 cm depth increment". The predicted amounts of NH_4^+ -N corresponding to the time (193:20) the last field measurement was made are given in Table 4, Appendix C. The data given in Table 4 are plotted in Figure 3-7. It is observed from Figure 3-7, that the

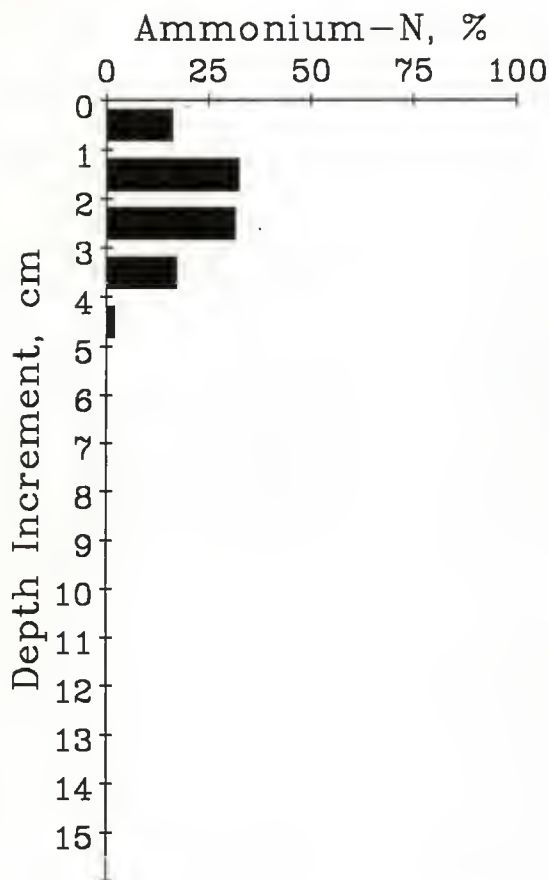


Figure 3-7. Modeled NH_4^+ -N distribution in soil at the time last field measurement for urea hydrolysis was made.

modeled distribution of $\text{NH}_4^+\text{-N}$ is a normal distribution as opposed to an even distribution, reported qualitatively, by McInnes et al. (1986).

In Chapter 1, soil pH was identified to be the master variable affecting soil equilibria. It is, therefore, expected that a comparison of modeled and field results for soil pH should be the most effective and reliable way to verify the model. Unfortunately, for this research, verification of the PC Model by a comparison of modeled and measured pH values is not possible because measurement of soil pH was not made for the field study undertaken by McInnes et al. (1986). Nevertheless, modeled results for soil pH are presented in Table 1, Appendix C, and in Tables 5 and 6, Appendix C. Data from Table 5 and 6 are plotted in Figures 3-8 and 3-9 respectively. As shown in Figure 3-8, pH in the 0-1 cm soil depth increment increased from an initial value of 6.4 to a maximum value of 7.0 on the day following the first irrigation (on 187:12). Subsequently, owing to the high ammonia-N losses during the time period between 187:12 to 195:18, the modeled surface pH was dropped to its initial level. From Chapter 1, it should be clear that the effect of ammonia volatilization is to lower soil pH. Since the simulated soil water content at the surface remained in the 1-3% (kg/kg basis) levels for a major time during the simulation (Fig. 3-3), little or no hydrolysis of urea occurred. Once again, from the theory discussed in Chapter 1, it should be clear that little or no HCO_3^- were produced at the surface. If diffusion of alkalinity toward the soil surface is relatively small, soil pH at the surface is expected to be lowered. The data of Ferguson and Kissel (1986) clearly shows that one of the effects of soil drying is a

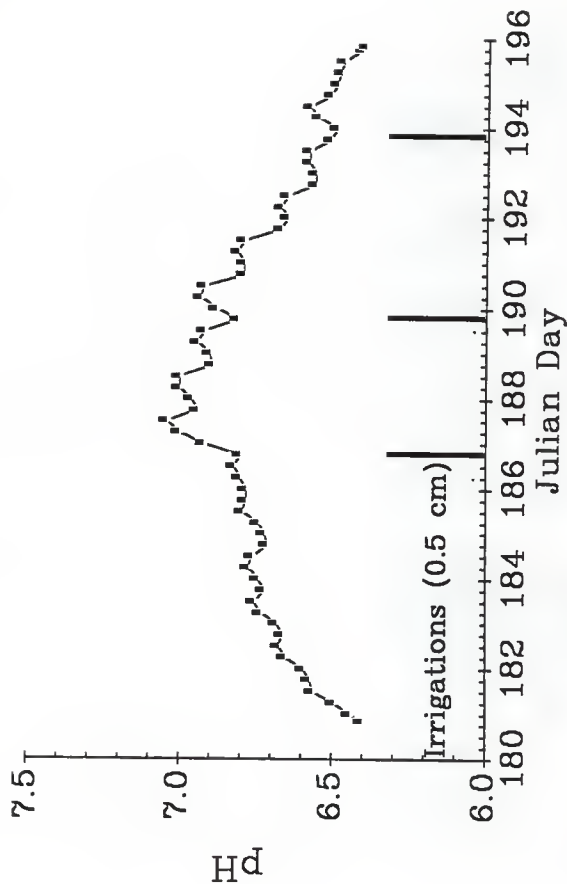


Figure 3-8. Modeled soil surface (0-1 cm depth increment) pH.

lowering of pH at the surface owing to ammonia volatilization. Figure 3-8 also illustrates the diurnal variations in soil pH at the surface. These variations are attributed to the variations in soil water content and temperature at the surface.

Another factor that influences soil pH is the H^+ buffering capacity of soil. Results of laboratory studies undertaken by Ferguson et al. (1984) show that the surface pH rose to a maximum value of 6.9 (Experiment 2, Soil Mix 3) and that the surface pH declined after a period of five days from the time urea was applied. Ferguson et al. (1984) mention that the "decline in soil surface pH after 5 days was due to the rate of loss of NH_3 by volatilization being greater than the rate of addition of NH_3 by hydrolysis after that time". The implication of this statement is that the rate of addition of H^+ to soil was faster than the rate of removal.

Figure 3-9 gives the initial and final soil pH profile. Figure 3-9 shows that in the 0 - 3 cm depth increment, soil pH remained above the initial pH while, in the 3-15 cm depth increment, soil pH was lowered below its initial value. An explanation of this result necessitates a consideration of the various sources and sinks for H^+ . In Chapter 1, a net sink term, $[H^+]_{sink}$, for H^+ balance was derived and defined by equation (1-42). Each of the terms comprising $[H^+]_{sink}$ were characterized by their tendency to raise or to lower the soil pH. It was found that the third, fourth and the last term in equation (1-42) or (1-43) were relatively insignificant. It should be noted that $[H^+]_{sink}$ is represented in the PC Model by equation (1-43).

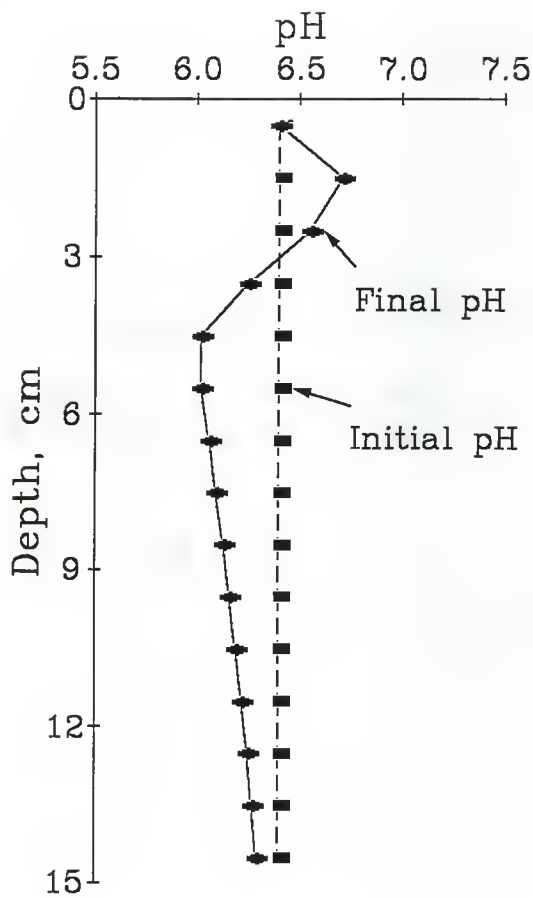


Figure 3-9 Modeled initial and final soil pH.

For H^+ -balance below the soil surface, the second term and the fifth term in equation (1-43) were omitted. Since these two terms account for the effect of $CO_{2(g)}$ loss and $NH_{3(g)}$ loss on soil pH, it is, therefore, assumed in the model that below the soil surface, for any given depth, the net loss of either $CO_{2(g)}$ or $NH_{3(g)}$ is zero. In reality, this assumption may not be true. In order to account for the effect on soil pH due to $CO_{2(g)}$ loss and $NH_{3(g)}$ loss, below the soil surface, it will be necessary to incorporate mass balances for $CO_{2(g)}$ and $NH_{3(g)}$ in the model.

The implication of the assumption, given above, is that soil pH below the surface is dictated by only two terms. These two terms are the first and the sixth terms in equation (1-43). The first term accounts for the effect on soil pH due to changes in the carbonate system equilibria which in turn is affected by urea hydrolysis. The sixth term accounts for the effect on soil pH due to soil respiration.

The modeled results for soil pH in the 0 - 3 cm depth increment and in the 3-15 cm depth increment can be explained as follows. Figure 3-4 shows that a considerable amount of urea is predicted to be present in the 0 - 3 cm depth increment subsequent to an irrigation event. It follows that the magnitude of the first term in equation (1-43) must be greater than the magnitude of the sixth term. This, in turn, implies that there is a net removal of H^+ in the 0 - 3 cm depth increment. Hence the modeled results for soil pH in the 0 - 3 cm depth increment are as expected.

It is further observed from Figure 3-9 that soil pH in the 3 - 15 cm depth increment is less than the initial pH. Figure 3-4 shows

that a relatively small amount of urea is present in the 3 - 4 cm depth increment and an insignificant amount in the 4 - 15 cm depth increment. It follows that for the 3 - 15 cm depth increment, the magnitude of the first term in equation (1-43) must be smaller than that of the sixth term. Hence, the modeled results show a lowering in soil pH for the 3 - 15 cm depth increment.

A limitation of the PC Model is that soil respiration rate is assumed to remain constant. The assumption is probably justifiable for the relatively small changes in air-filled porosity owing to diurnal variations in soil water content. However, subsequent to an irrigation event, the air-filled porosity of soil may be drastically reduced from 50% levels to levels less than 20%, especially, in the 0-5 cm depth increment where a significant infiltration of soil water occurs. Despite a significant decrease in the air-filled porosity of soil, soil respiration rate is assumed to remain constant. In reality, however, the concentration of oxygen in soil air will increase in response to a decrease in air-filled porosity. It is, therefore, expected that soil respiration rate will be affected by an increase in the concentration of oxygen. In discussing the effect of oxygen concentration on soil respiration rate, Campbell (1985) points out that "in soil profiles, resistances to diffusion to sites of respiration may cause respiration rates to fall at higher concentrations". Based on the observation of Campbell (1985), it is concluded that, if the soil respiration rate is assumed to be constant the modeled results for soil pH will be in error in the event soil air-filled porosity is low (less than 20%).

The previous discussion suggests that the predicted lowering of soil pH, in the 3 - 4 cm depth increment, may be greater than that in reality. Figure 3-9 also shows that in the 4 - 15 cm depth increment, lowering of soil pH decreases with depth. This result is expected in view of the fact that, in the PC Model, soil respiration is defined to decrease exponentially with depth.

Verification of the model may also be made in terms of the predicted partial pressures of $\text{NH}_3(\text{g})$ and $\text{CO}_2(\text{g})$ in soil air. In Figures 3-10 and 3-11, the partial pressures of $\text{CO}_2(\text{g})$ and $\text{NH}_3(\text{g})$, in the soil air of the surface layer of soil (1 cm depth increment), are plotted as a function of time. Data for Figures 3-10 and 3-11 are given in Table 5, Appendix C. Measurements for $\text{CO}_2(\text{g})$ and $\text{NH}_3(\text{g})$ partial pressures were not made during the field study. However, Singh and Nye (1986) mention that in the surface soil layers, partial pressures of $\text{CO}_2(\text{g})$ are generally found to be in the range 0.002 - 0.005 atm. An examination of Figure 3-10 reveals that the predicted partial pressures of $\text{CO}_2(\text{g})$ lie in the range 0.0008 - 0.0037 atm. The partial pressures of $\text{NH}_3(\text{g})$ in soil air have been measured by Blanchar (1967) at different soil pH values. In the soil pH range of 6.18 to 7.13, the measured values of $\text{NH}_3(\text{g})$ partial pressures were found to be in the range of 0.004 - 0.0072 mm Hg. In comparison, the modeled values for the partial pressures of $\text{NH}_3(\text{g})$ are observed, from Figure 3-11, to range from zero to 0.00085 mm Hg. The predicted $\text{NH}_3(\text{g})$ partial pressures are considerably lower than the measured values reported by Blanchar (1967). It should, however, be noted that the measured values of $\text{NH}_3(\text{g})$ partial pressures were obtained in the absence of $\text{CO}_2(\text{g})$.

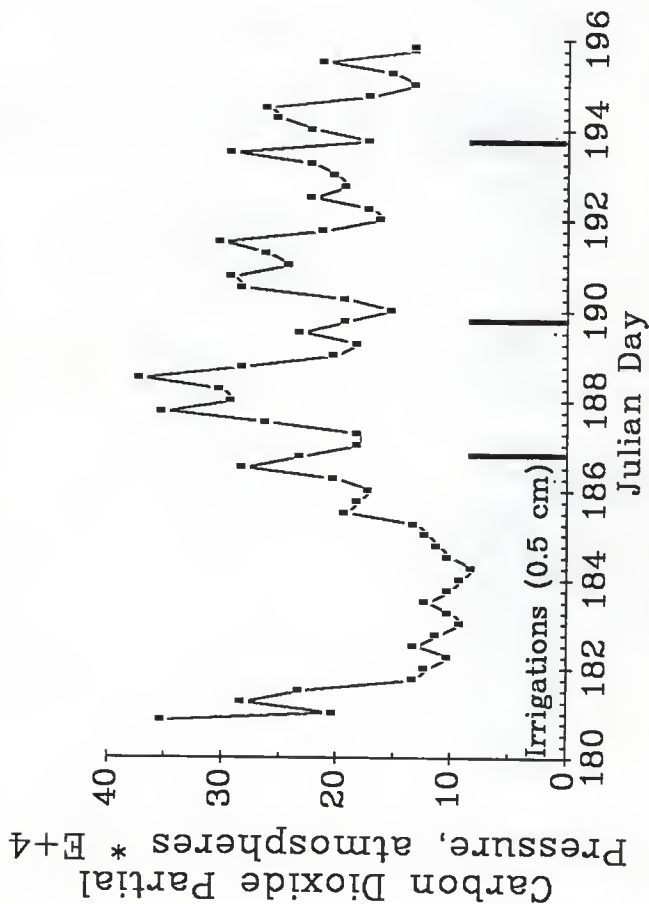


Figure 3-10. Modeled carbon dioxide concentration in the soil air of soil surface (0-1 cm depth increment).

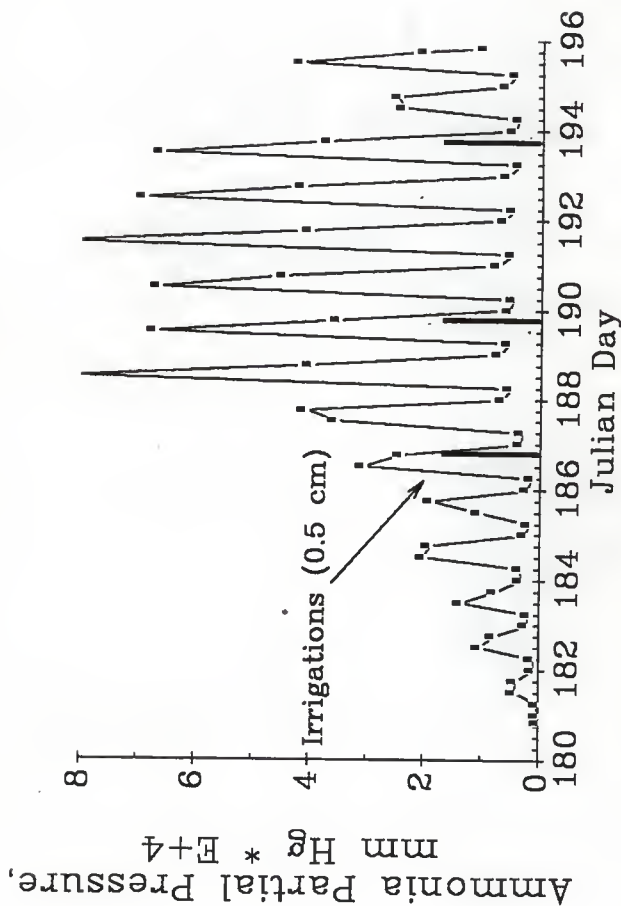


Figure 3-11. Modeled ammonia concentration in the soil air of soil surface (0-1 cm depth increment).

Further, the soil depth used for measurements is not specified. Since the model predicted a greater amount of NH_4^+ to be present in the 1-3 cm depth increment than in the 0-1 cm depth increment, it is expected that the predicted $\text{NH}_{3(g)}$ partial pressures in the 1-3 cm depth increment will also be greater. Blanchar (1967) points out that theoretically, "a pH decrease of 0.25" due to an increase in $\text{CO}_{2(g)}$ partial pressure from 0.0014 to 0.0025 atm, "would result in a drop in the partial pressure of $\text{NH}_{3(g)}$ by 56%". Blanchar (1967) goes on to add that the theoretical decrease in the partial pressure of $\text{NH}_{3(g)}$ "is a much larger decrease than occurred". Nevertheless, in the presence of $\text{CO}_{2(g)}$, the partial pressures of $\text{NH}_{3(g)}$ are expected to be significantly lower. The $\text{NH}_{3(g)}$ solubility data given by Hales and Drewes (1979) suggest that the solubility of $\text{NH}_{3(g)}$ may increase by as much as one order of magnitude in the presence of $\text{CO}_{2(g)}$. This, in turn, implies that the partial pressure of $\text{NH}_{3(g)}$ may be lowered by as much as one order of magnitude in the presence of $\text{CO}_{2(g)}$. Hence, it may be argued that the modeled partial pressures of $\text{NH}_{3(g)}$, obtained for this research, may be realistic. Final verification of the model is made in terms of the measured and modeled soil surface temperature. As shown in Figure 3-12, a reasonably close agreement was obtained. Data for Figure 3-12 are given in Table 8, Appendix C.

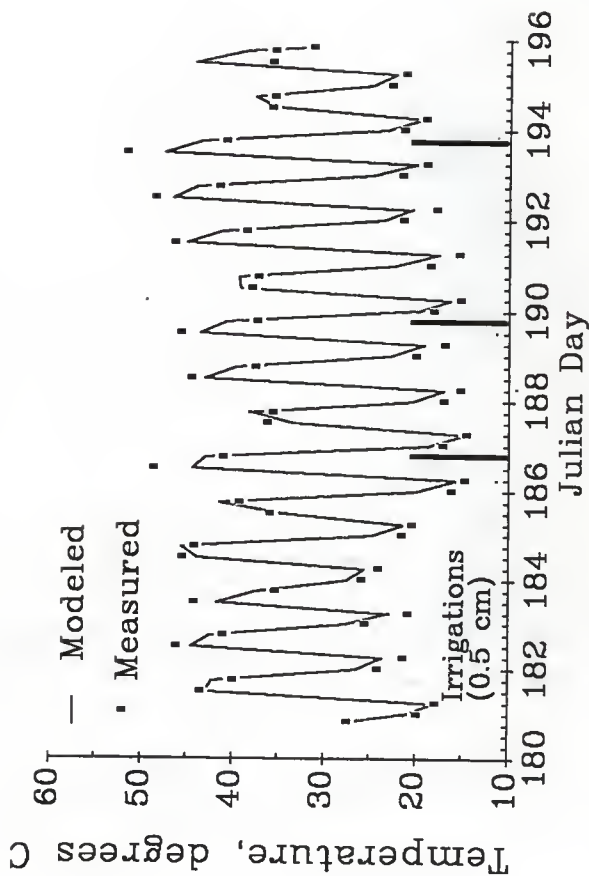


Figure 3-12. Modeled and measured soil surface (0-1 cm depth increment) temperature.

Sensitivity Analysis

The modeled results discussed in this chapter were obtained for a standard set of values for the sensitivity parameters. These values are listed as part of the computer output of results (Table 1, Appendix C). The PC Model was tested for the following sensitivity parameters:

IPH = initial soil pH, considered to be constant for the entire soil depth.

TCA = total Ca^{2+} , mg/kg soil

OCARB = organic carbon content of soil, %

APRATE = application rate of urea, kg urea-N/ha

SRESP = soil respiration rate at the surface, $\text{kmol}/(\text{m}^3)(\text{s})$

NK1 = coefficient of the Freundlich equation for the adsorption isotherm of NH_4^+ , dimensionless

FOO2 = a correction factor for $\text{CO}_{2(g)}$ solubility, dimensionless

FNH3 = a correction factor for $\text{NH}_{3(g)}$ solubility, dimensionless

FSBC = a multiplying factor for varying soil buffering capacity, dimensionless

FRAC = gas-film mass transfer resistance for $\text{CO}_{2(g)}$ expressed as a fraction of the overall mass transfer resistance, dimensionless

SCO2 = initial concentration of $\text{CO}_{2(g)}$ in soil air, kmol/m^3 soil air

Simulated results for sensitivity of the PC Model are summarized in Table 7. Each set of results was obtained by varying the standard set value of a sensitivity parameter while retaining the standard set values of the other sensitivity parameters. The data of Table 7 are plotted in Figures 3-13 and 3-14.

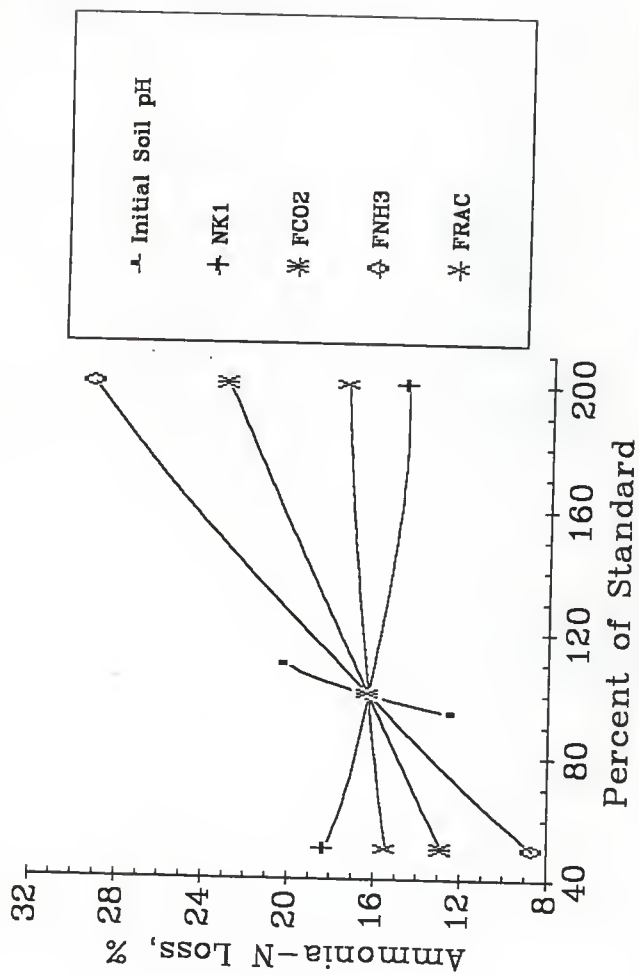


Figure 3-13 Sensitivity Analysis: Effect of initial soil pH, ammonium adsorption, carbon dioxide solubility, ammonia solubility and resistance to mass transfer of carbon dioxide on ammonia volatilization loss.

The results given in Table 9 show that the model is very sensitive to the value of IPH. Ammonia-N loss (LOSS) decreased by approximately 24.5% when the standard set value of IPH was reduced by 6.25%. On the other hand, when the standard-set value of IPH was increased by about 9.4%, LOSS increased by 23.1%. The model showed greater sensitivity to a lower initial soil pH.

Table 7 also shows that the model is almost insensitive to TCA. In fact, when the value of TCA was taken to be either one-half or two times the standard-set value of TCA, the results for percent urea hydrolyzed (UHYD) and LOSS were found to be identical to the standard set results.

The model showed significant sensitivity to the value of OCARB. A 50% decrease in OCARB resulted in a 17.6% decrease in the value of LOSS while, a 100% increase in the value of OCARB led to a 19.8% increase in the value of LOSS.

When APRATE was taken to be twice its standard set value (a 100% increase), the value of LOSS increased by only 22.8%. On the other hand, when the value of APRATE was halved, the value of LOSS decreased by 21.8%. Since Michaelis-Menten type of relation is used to describe urea hydrolysis rate, it should be obvious that an increase (or a decrease) in urea concentration will not lead to a directly proportional increase (or a decrease) in urea hydrolysis rate. Hence, it is expected that the magnitude of LOSS will not be directly proportional to the value of APRATE. It should be noted that in order to compute the percent increase in LOSS, the $\text{NH}_3\text{-N}$ LOSS value, given in Table 7, was multiplied by two. On the other hand, the table value

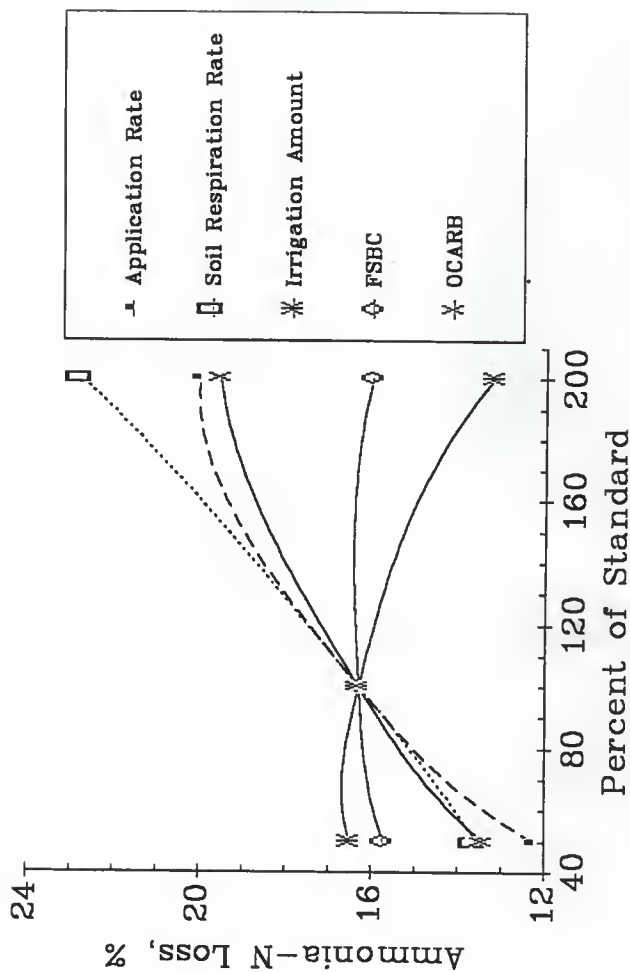


Figure 3-14 Sensitivity analysis: Effect of urea application rate soil respiration rate, amount of irrigation, hydrogen-ion buffering capacity of soil and organic carbon content of soil on ammonia volatilization loss.

of $\text{NH}_3\text{-N}$ LOSS was divided by two to compute the percent decrease in LOSS.

Table 7 further shows that when the value of NKl was doubled, a relatively small decrease of 9.9% in the value of LOSS resulted. An examination of the maximum and minimum (MAX/MIN) values of soil pH reveals that since the surface soil pH remained relatively high, even a 100% increase in the value of NKl could not significantly curtail $\text{NH}_3(\text{g})$ loss. It is also observed from Table 7 that when the value of NKl was decreased by 50%, the value of LOSS increased by only 11.9%. Owing to the highly non-linear relationship between NH_4^+ in solution and in the adsorbed phase, the sensitivity of the model to the value of NKl is as expected.

The model was found to be very sensitive to the value of FNH_3 and, to a lesser degree, to the value of FCO_2 .

A 100% increase in the value of FCO_2 resulted in a 41% increase in the value of LOSS, while a 50% decrease in FCO_2 was responsible for a 21.3% decrease in LOSS. Since the model considers the solubility of $\text{CO}_2(\text{g})$ to vary in with the value of FNH_3 . Thus, a decrease in the value of FNH_3 implies an increase in the solubility of $\text{NH}_3(\text{g})$, resulting in a decrease in the concentration of $\text{NH}_3(\text{g})$ in soil air. Hence, it is concluded, that modeled results for sensitivity to FNH_3 are as expected. direct proportion with the value of FCO_2 , the amount of HCO_3^- in solution increases with increase in the value of FCO_2 . Increase in HCO_3^- concentration leads to an increased surface soil pH and hence, results in an increased $\text{NH}_3(\text{g})$ loss.

The sensitivity of the model to FSBC is, probably, debatable. As shown in Table 7, an increase in the value FSBC led to a relatively small decrease. A possible explanation for the result predicted by the model is that owing to the increased H^+ -buffering capacity of soil, the soil surface pH was not lowered as much as it was for the standard set value of FSBC. Thus, despite the fact that the surface pH did not rise as much as it did for the standard set value of FSBC, the surface pH remained higher during the latter part (day 190 to day 193) of simulation when ammonia flux losses are higher. It is, therefore, conceivable that the total ammonia-N loss turned out to be relatively high for increased soil buffering. The result obtained for this research suggests that the effect of soil buffering capacity on soil pH may be masked by other dominating factors such as low surface soil water content and high surface temperatures.

When H^+ -buffering capacity of soil was taken to be half of the standard set value a decrease in $NH_3(g)$ loss occurred. An examination of the MAX/MIN values of soil pH shows that although the rise in soil pH was slightly greater than that for the standard set, results the drop in pH was more pronounced. Therefore, a relatively lower surface pH, during the latter part of the simulation, was responsible for a lower overall $NH_3(g)$ loss.

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The sensitivity of the model to parameter FRAC was according to expectations. An increase in the value of FRAC results in less resistance to mass transfer of $CO_2(g)$ from the soil surface. Accordingly, the soil surface pH is expected to rise more for an increase in the value of FRAC over its standard set value. Table 7 shows that indeed the surface pH rose somewhat more compared to the standard set results. Therefore, a relatively higher surface pH led to a relatively higher $NH_3(g)$ loss. An opposite result was obtained, as expected, when the value of FRAC was taken to be half the value of the standard-set. The pH did not rise as much and also the drop in pH

was more than that for the standard set results. Hence, a relatively lower surface pH was responsible for a lower $\text{NH}_{3(g)}$ loss.

The sensitivity of the model to parameter SRESP may be questionable. Singh and Nye (1986) report an insignificant change in $\text{NH}_{3(g)}$ loss by a three-fold variation, on each side, in the soil respiration rate. It should, however, be noted that the Singh and Nye - model does not consider variations in soil water content and soil temperature with respect to space and time. Further, convective transport is not included in the Singh and Nye-model. A third difference is due to the fact that a separate mass balance for $\text{CO}_{2(g)}$ is made in the Singh and Nye-model. In the PC Model, as shown in Chapter 1, mass balances for all carbonate species are lumped into a single equation where concentrations of all carbonate species are expressed as a ratio of the concentration of HCO_3^- . Since soil respiration is incorporated in the equation, as a source term, it is conceivable that variations in soil respiration rate will have a pronounced effect on the concentration of HCO_3^- and, hence, on pH. Further, due to the dynamic nature of the PC Model, the assumption of a constant soil respiration rate may be in error, especially, at low (less than 20% air-filled porosity) of soil.

A final check for model-sensitivity was made in terms of the amount of irrigation water applied. It may be recalled that 0.5 cm of water was applied for each of the three irrigations carried out during the field study. The model was tested first, by simulating application of 0.25 cm of water for each of the three irrigations, then by

a simulated application of 1.0 cm of water for each irrigation and finally, by simulating a one-time application of 2.54 cm of irrigation water, four hours after application of urea.

Table 7 shows that for a simulated application of 0.25 cm of irrigation water $\text{NH}_3(\text{g})$ loss increase slightly compared to the standard-set result. The increase in the value of LOSS occurred despite the fact that only 78.9% of the applied urea hydrolyzed. The result shows that, as in the case of the standard-set results, irrigation tended to enhance ammonia volatilization loss.

The modeled results show that, when application of irrigation water was taken to be twice as much as the standard irrigations, the value of LOSS decreased but not significantly. The relatively high $\text{NH}_3(\text{g})$ loss of 13.2% may be attributed to a faster urea hydrolysis rate owing to an increased soil water content, and to a relatively higher surface soil pH.

It is generally perceived that application of 2.54 cm of irrigation water will result in a minimal or a negligible $\text{NH}_3(\text{g})$ loss. A sensitivity test of the model for a 2.54 cm application of irrigation water revealed that approximately, 7.3% of the applied urea-N was lost due to ammonia volatilization. Since a considerable amount of urea was predicted to be present in the lower soil depth increments, the $\text{NH}_3(\text{g})$ loss was relatively low despite the fact that 100% of the applied urea was hydrolyzed with 2 days. However, owing to soil surface drying, urea was transported back to the soil surface by both diffusive and convective transport. It is, therefore, understandable

why ammonia volatilization losses were not eliminated by an application of, as much as, 2.54 cm of irrigation water.

Conclusions and Recommendations

A generalized computer model has been developed to simulate transport of urea and to predict ammonia volatilization loss under field conditions for surface application of urea. The model was developed on a Personal Computer (PC) using Microsoft FORTRAN as the programming language. With minimal change in computer code, the model may be adapted to an IBM 370 system using FORTRAN 77 as the programming language.

A time-step of 5 minutes was used in the model. It was determined for this research that a time step greater than 5 minutes led to instability in the model. For a 15-day meteorological data set spaced at 5-minute intervals, simulated results for 15 soil depth increments (15 nodes) were obtained in 18-24 hours on a PC equipped with a numeric co-processor and 640 K RAM. A total of 48 nodes may be presently used in the simulation. If a greater number of nodes are found to be necessary, parameter L, in the model, will need to be increased. This will necessitate recompilation of the source program and relinking of the object module.

A total of 24 sets of simulated results, including the standard-set result, were obtained for the PC model using the same, 15-day meteorological data set. It is concluded that the model has been carefully debugged and is expected to run for any set of parameter values, soil characteristics and meteorological data. A maximum time

step of 5 minutes is recommended for any meteorological data set to be used by the model.

The model developed for this research represents an attempt to simulate a complex system which is acted upon by many environmental factors. Despite the complexity of the system being modeled, the modeled ammonia-N loss of 16.3% compares favorably with the field loss of 17% reported by McInnes et al. (1986). Owing to inadequacy of field data, a more thorough comparison of modeled and field results was not possible. It is, therefore, recommended that future efforts directed toward improving the present model should also include a field study on ammonia volatilization. One shortcoming of the field study of McInnes et al. (1986) was that measurements for soil pH were not made. The theory of ammonia volatilization, discussed in Chapter 1, clearly points out the significance of pH in affecting the equilibria of various chemical reactions. It was also determined from sensitivity analysis of the model that ammonia volatilization loss was influenced to a significant degree by soil pH, particularly by the surface pH. It is, therefore, strongly recommended that future field studies on ammonia volatilization must be designed so that measurements of soil pH be made without altering the soil water content of the soil sample. A preferred measurement technique will require a sensitive pH meter with a probe so that insitu pH measurements are made at pre-determined soil depths. In fact, it is recommended that as far as possible, insitu measurements for NH_4^+ , HCO_3^- , Ca^{2+} and urea be made.

It is emphasized that the soil profile used in the model must correspond to the depths be chosen in a field study. It should be noted that the model provides flexibility to change the total depth as well as the total number of soil depth increments (number of nodes). Hence, the chosen depth intervals used in the model may be changed according to the depth intervals to be used in a field study. There are two restrictions to choosing depths in field-measurement: (i) the total depth must be greater than or equal to 6 cm but less than or equal to 30 cm; (ii) the soil depths must be spaced at equal intervals.

It is also recommended that a detailed log of all field measurements be kept. In particular, when field results are presented in graphical form, graphical data should be accompanied by tabulated data or a reference be provided to obtain it. A second shortcoming of the field results reported by McInnes et al. (1986) was that tabulated results are not given for field measured values of soil water content, urea hydrolyzed, and $\text{NH}_{3(g)}$ loss. It is further recommended that field results be reported in a way that all references to soil depth increments be clearly stated. For example, McInnes et al. (1986) measured NH_4^+ in field and reported that "there was almost an equal distribution in the surface 4 cm" The depth increments used to arrive at the conclusion that the distribution was uniform are not specified. This type of reporting of field results poses a problem to a modeler who, at best, can only speculate under such circumstances.

Results for the sensitivity analysis of the model, summarized in Table 7, clearly show that the model is sensitive to the values of the following parameters: IPH, APRATE, OCARB, SRESP, NK1, FCO2, FNH3,

FSBC and FRAC. The model also showed sensitivity to the simulated applications of irrigation water. In fact, ammonia volatilization loss was influenced the most by the simulated application of 2.54 cm of irrigation water. It should be noted that in order to test the model for sensitivity to a simulated application of 2.54 cm of irrigation water, the total modeled soil depth was increased to 30 cm and the number of nodes was increased to 30. Despite this change, the distance between the nodes (depth of a soil layer) was kept the same (1 cm) as for the standard set of parameter values. It is recommended that when testing the model for increased applications of irrigation water, a total soil depth equal to 30 cm be used.

The results obtained for model-sensitivity to FNH_3 and FCO_2 suggest that the predicted $\text{NH}_{3(g)}$ loss is strongly influenced by the solubilities of $\text{NH}_{3(g)}$ and $\text{CO}_{2(g)}$ in soil solution. In the heterogeneous system consisting of soil, soil air and soil solution, the solubilities of $\text{NH}_{3(g)}$ and $\text{CO}_{2(g)}$ are expected to be significantly different from their measured solubilities in pure water at atmospheric pressure. For the standard-set results, (16.3% ammonia-N loss), the solubilities of $\text{NH}_{3(g)}$ and $\text{CO}_{2(g)}$ were assumed to be one-tenth and ten times respectively, of their respective solubilities in pure water at atmospheric pressure. The assumptions made for the solubilities of $\text{NH}_{3(g)}$ and $\text{CO}_{2(g)}$ need to be verified. The assumptions may be verified by measuring the partial pressures of $\text{NH}_{3(g)}$ and $\text{CO}_{2(g)}$ in soil air in the presence of each other, at vary soil pH-values, and in the presence of all chemical species considered in the model.

The modeled results for sensitivity to soil respiration rate, suggest that the assumption of a constant soil respiration rate, for a given soil depth, may be in error particularly after an irrigation event. It is, therefore, recommended that a subroutine to predict soil respiration rate, be incorporated in the model. Since determining the parameters for predicting soil respiration rate may require considerable work, it is recommended that for the present, a constant soil respiration rate may be retained in the model. However, a field-measured rate should be used, with measurements made at varying depths, so that the respiration rate for a given depth is correlated to the surface respiration rate.

In the PC Model, the initial soil pH was taken to be the same for the entire modeled soil depth. In view of the fact that soil respiration tends to lower soil pH, the soil layers below the surface layer are expected to have a lower initial soil pH. Since the model showed considerable sensitivity to the initial soil pH, it is recommended that measurements for initial soil pH be made upto a depth of 15 cm. This would allow a more realistic soil pH profile to be used in the model for the initial conditions.

Considerations for the equilibria of the ammonia system suggest that increased NH_4^+ adsorption will tend to increase the solubility of $\text{NH}_3(\text{g})$ and decreased adsorption will tend to have an opposite effect on the solubility of $\text{NH}_3(\text{g})$. In view of the sensitivity of the model to the solubility of $\text{NH}_3(\text{g})$, it is recommended that a more fundamental understanding be developed for the cation-exchange process between NH_4^+ and Ca^{2+} . Further, an equation to describe the cation-exchange

mechanism between NH_4^+ and H^+ should be incorporated in the model. It may be of interest to consider the use of the Gapon equation to relate NH_4^+ in the adsorbed phase to NH_4^+ in solution. The use of the Gapon equation in the model necessitates the need to obtain consistent data for the prediction of the values of the Gapon constant. The Freundlich equation should be retained in the model until satisfactory values of the Gapon constant are experimentally determined and correlated to temperature. The use of the Freundlich equation makes it necessary to obtain a reasonable estimate of the two empirical constant in the equation. It should be noted that for the standard results presented in this research, the value of the exponent in the Freundlich equation was taken to be the value (0.66) given by the data of Singh and Nye (1986). The value of the other constant was taken to be the average of the value given by Singh and Nye (1986) and the value obtained by a graphical fit of the data, for Parsons soil, given by Izaurrealde (1985). Once again, the evaluation of the constants for the Freundlich equation dictates a need to obtain consistent data relating NH_4^+ in the adsorbed phase to NH_4^+ in soil solution.

The model showed an uncharacteristic sensitivity to soil buffering capacity. However, the uncharacteristic behavior of the model may be attributed to high surface temperatures (which enhance ammonia volatilization) and extreme loss levels of surface soil water content for a major time period of the simulation. Owing to soil drying, the concentration of NH_4^+ increases with a consequent increase in the upward flux of ammonia, resulting in an increased $\text{NH}_3(\text{g})$ loss. Since $\text{NH}_3(\text{g})$ loss tends to lower soil pH, increased soil buffering

capacity reduces the lowering in soil pH and is, therefore, responsible for the higher $\text{NH}_3(\text{g})$ loss predicted by the model for increased soil buffering capacity. A similar argument applies to the lesser $\text{NH}_3(\text{g})$ loss predicted by the model for a decrease in soil buffering capacity.

The sensitivity-analysis results presented by Singh and Nye (1986) showed an increase in $\text{NH}_3(\text{g})$ loss for a decrease in soil buffering capacity. A much higher soil water content at the surface (20% on a weight-basis) and a moderate temperature (25°C), both assumed to remain constant in space and time, are the fundamental factors for the discrepancy in the sensitivity of the two models (PC Model, Singh & Nye-model) to soil buffering capacity. A further difference in the two models is that convective transport of solute is excluded from the Singh and Nye-model while in the PC Model, mass transfer by convection is considered. Nevertheless, it is recommended that the soil buffering capacity data (for Haynie soil), given in the Annual Report (1985) and used in the present research to develop the soil buffering capacity equation, should be verified.

The sensitivity of the model to parameters FRAC suggests a need to determine the resistance to mass transfer for $\text{CO}_2(\text{g})$ by an empirical method. For the present research, parameter FRAC was determined to be the value that yielded a reasonable pH profile for the modeled soil depths based on a negligibly small (0.01 kg urea-N/ha) simulated application of urea. Since the soil profile considered to be reasonable cannot be verified, it is recommended that in a future field study on ammonia volatilization, measurements for

soil pH at varying depths be made for a microplot on which urea fertilizer is not applied. The value of FRAC that yields a modeled soil pH profile in reasonable agreement with the measured pH profile may be considered to be the empirically determined value of FRAC. Alternatively, by measuring $\text{CO}_2(\text{g})$ loss in the same way as $\text{NH}_3(\text{g})$ loss is measured, the resistance to mass transfer for $\text{CO}_2(\text{g})$, may be correlated to the resistance to mass transfer for $\text{NH}_3(\text{g})$.

McInnes (1985) gives a field measured value for the organic matter content of Haynie soil to be 0.8%. However, the standard-set value for the organic carbon content of Haynie soil was taken to be 1.04% upon the advice of Kissel (1987) so that computed values of v_{max} would be the same as measured. The sensitivity of the model to the value of OCARB suggests a need to accurately measure the organic matter content of soil and to compute the organic carbon content from the measured value of organic matter content.

Many researchers have pointed out the inaccuracies involved in the use of interpolated and extrapolated data. For the present research, meteorological data was interpolated between 184:17 and 185:9. Also the meteorological data for the time period 195:12 to 195:20 was considered to be identical to that for the time period 194:12 to 194:20. These steps were taken simply because data for these time periods were either incomplete or not available. It is necessary to carefully evaluate any data used in a model. In the present research, the surface temperature data, for a certain period of the field study undertaken by McInnes et al. (1986), were found to be erroneous and the erroneous data were replaced by interpolated values.

The soil buffering capacity equation developed for this research is based on data obtained for a pH range of 6.24 to 8.53. Since the modeled soil pH was lowered to levels below 6.24 for some of the sensitivity-analysis results, it is obvious that extrapolated data were used. Thus, there is a possibility of error in the modeled results for pH values less than 6.24. In view of the errors associated with the use of extrapolated data, it is recommended that all laboratory and field measurements for soil properties, characteristics, diffusivities of solutes, equilibrium constants and other necessary data should be determined over a range of values for temperature, soil water content and pH, expected to be used in the model.

Implementation of the recommendations made thus far is considered to be necessary to the success of efforts to model ammonia volatilization under field conditions. The recommendations that follow are not considered to be critical to the success of the model but may be considered as improvements to the model. A first recommended improvement to the model may be accomplished by using activities instead of concentrations for all chemical species. A second recommended improvement is to incorporate charge-balance along with mass balances. In order to incorporate charge-balance in the model, it may be necessary to include other chemical species, such as chloride ions, which are presently not included in the mass balances. It is also recommended that solubilities of $\text{NH}_3(\text{g})$ and $\text{CO}_2(\text{g})$ be based upon charge-balance considerations. A final recommendation for future efforts to improve the present model relates to the finite differencing scheme used to represent the partial differential equations that govern the transport

of heat, mass and momentum. It is recommended that instead of the weighted-average scheme used in the present research, a Crank-Nicholson scheme, as given by Bressler (1973), be used. The finite difference equations, given by Bressler (1973), incorporate mass transfer by dispersion, numerically, and thus eliminate the need to measure dispersion coefficients for the chemical species considered in the model. It may also be of interest to investigate an alternate method to solve the finite difference equations, either by changing the structure of the model, or by using a new method of solution. The Newton-Raphson Method, used in the present research, is efficient in solving heat and momentum transport equations. However, owing to the structure of the present model, solution of the mass-balance equations is not efficient because the values of partial derivatives ($\partial/\partial C$) used in mass balance equations do not change with iteration. This is so because the partial derivatives are primarily a function of diffusivity which in turn is taken to be a function of temperature. Owing to the structure of the model, since, temperature does not change with iteration in the solution of mass balances. Hence convergence for mass balances is slow.

APPENDIX A

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APPENDIX B

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C THIS MODEL SIMULATES AMMONIA VOLATILIZATION UNDER FIELD CONDITIONS
C FROM APPLICATION OF UREA TO SOIL SURFACE.
C DEVELOPED BY HASAN JAFAR, GRADUATE STUDENT, DEPARTMENT OF CIVIL
C ENGINEERING, KANSAS STATE UNIVERSITY, MAY 1988
C
SDEBUG
SNOFLOATCALLS
$STORAGE:2
C
    IMPLICIT REAL*8 (A-Z)
    INTEGER*2 I,J,L,M,N,JJ,KK,ITER,DT,FLAG,MFLAG,NFLAG,COUNT,DAY,
1    HOUR,MIN
    LOGICAL*2 FCLOSE
    PARAMETER (L=50,R=8.314)
    DIMENSION NCA(L),NH(L),NHCO3(L),NCAAD(L),NNH4AQ(L),NCALC(L),
1    UCAAD(L),UCA(L),ADS(L),NADSH(L),HRESP(L),HCALC(L),HSINK(L),
1    UHC(L),UHN(L),P1(L),P2(L),P4(L),P5(L),P6(L),P8(L),P9(L),P10(L),
1    P11(L),P12(L),P13(L),P14(L),JCALC(L),JHCO3(L),JCO2AQ(L),JH(L),
1    JNH4AQ(L),JHCO3(L),ACA(L),AH(L),AOH(L),ACO3(L),ACO2AQ(L),HADS(L),
1    ACALC(L),ANH3AQ(L)
C
    COMMON /BLK0/U(L),ANH4AQ(L),AUAQ(L),PERUH,LOSS,HYD,SHYD
1    /BLK1/Z(L),VOL(L),P(L),FA(L),POROS(L),CAP(L),D(L),TOTALU
1    /BLK2/PH(L),MASS(L),FLAG,RESPIR(L)
1    /BLK3/A(L),B(L),C(L),F(L),MAXVAL,MINVAL,NFLAG
1    /BLK5/NH4AQ(L),NH3AQ(L),HCO3(L),CO2AQ(L),H(L),MU(L),CA(L)
1    /BLK7/TAIR,VDA,UHM,RA,RH,PCP,PA(L),PN(L),AW(L),VDS(L),S(L),
1    DWV(L),WAP(L),TA1(L),RNH3P,RNH3,JA(L),JB(L),JC(L)
1    /BLK8/T(L),TA(L),TN(L),W(L),WA(L),BD(L),TSURF,HOUR,DAY,MIN
1    /BLK9/MW,LHV,PAE,B1,SAND,SILT,CLAY,KSAT(L),B2,AT,BT,HT,
1    XT,CT,PDRAIN,KVP(L),KVT(L),KW(L),KH(L),EVAP,RAIN,
1    PRECIP,JW(L),JWC(L),ERR(L),FH,FU,FW,FO,GH,GU,GW,GO
1    /BLK10/M,N,JJ,OCARB,DT,TDEPTH
1    /BLK11/NH4AD(L),NH4CO3(L),N4HCO3(L),NH3G(L),NH3LOS,CO2LOS
1    /BLK12/INH4AQ(L),INH3AQ(L),INH4AD(L),INH3G(L),INH4C3(L),IH(L),
1    IN4HC3(L),ICO2AQ(L),IHCO3(L),ICO3(L),ICO2G(L),ICALC(L)
1    /BLK13/CO3(L),CO2G(L),CALC(L),NYIELD,CYIELD,NRECOV,CRECOV,HGEN
1    /BLK14/ADSH(L),HINIT,CAINIT,DNH4AQ(L),DHCO3(L),DNH3AQ(L),
1    DCO2AQ(L),DCO2G(L),DNH3G(L),CAACT,HACT,IADSH(L),CAAD(L)
C
    DEFINE FUNCTIONS FOR EQUILIBRIUM CONSTANTS
    *****
    K0(TT)=10.0**(-4470.99/TT+6.0875-0.017060*TT)
    K1(TT)=(10.0**((1477.7/TT-1.69)))/FNH3
    K2(TT)=10.0**(-2729.92/TT-0.09018)
    K4(TT)=1.45
    K5(TT)=4.54D-2
    K7(TT)=10.0**((2385.73/TT-14.0184+0.0152642*TT)*0.08206*TT*FCO2
    K8(TT)=10.0**(-3404.71/TT+14.8435-0.032786*TT)
    K9(TT)=10.0**(-2902.39/TT+6.498-0.02379*TT)
    K11(TT)=10.0**((2.06283+429.281/TT-2.07849*LOG(TT)))
    K12(TT)=10.0**((1658/TT-22.56))
C
    DEFINE FUNCTIONS FOR DIFFUSION COEFFICIENTS IN WATER AND AIR
    *****
    D1(TT)=1.56D-10*TT-3.73D-8
    D2(TT)=1.26D-10*TT-3.22D-8
    D4(TT)=1.84D-5+1.40D-7*TT
    D5(TT)=1.4168D-8+5.5345D-11*TT

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```

WRITE(5,40)
40  FORMAT(/1X,'IPH',2X,'TCA',2X,'OCARB',1X,'APRATE',1X,'SRESP',4X,
1  'NK1',4X,'NK2',2X,'FCO2',2X,'FNH3'3X,'FSBC',3X,'FRAC',3X,'SCO2')
WRITE(*,50)IPH,TCA,OCARB,APRATE,SRESP,NK1,NK2,FCO2,FNH3,FSBC,
1  FRAC,SCO2
WRITE(5,50)IPH,TCA,OCARB,APRATE,SRESP,NK1,NK2,FCO2,FNH3,FSBC,
1  FRAC,SCO2
50  FORMAT(F4.1,F6.0,1X,F4.2,3X,F4.0,1X,E7.2,1X,E7.2,1X,F4.2,2X,F4.1,
1  2X,F4.1,3X,F4.2,2X,F5.4,1X,E7.2)

C
C  DEFINE SOIL NODES
C  *****
Z(1)=0.0
Z(2)=0.0
DO 60 I=3,KK
Z(I)=Z(I-1)+DZ
60  CONTINUE

C
C  READ SOIL CHARACTERISTICS AND ASSUMED INITIAL CONDITIONS
C  *****
READ(4,*)(BD(I),I=1,M)
READ(4,*)(W(I),I=1,M)
READ(4,*)(T(I),I=1,M)
READ(4,*)B1,PAE,PDRAIN,SAND,SILT,CLAY,AT,BT,HT,XT,A1,A2,A3,A4

C
C  DEFINE AND INITIALIZE OTHER SOIL RELATED PROPERTIES
C  *****
PCP=1200.
MW=0.01802
LHV=2.43D6
B2=2.0+3.0/B1
CT=((XT-1.0)/XT)**(1.0/XT)*(-800.0/PAE)**(1.0/B1)
KVP(1)=0.0
KVT(1)=0.0
KW(1)=0.0
KH(1)=0.0
JW(1)=0.0
EVAP=0.0
PRECIP=0.0
RAIN=0.0
TOTALU=APRATE/(28.0134*1.0D4)

C
C  WRITE SOIL CHARACTERISTICS AND ASSUMED INITIAL SOIL PROPERTIES
C  *****
WRITE(*,70)
WRITE(5,70)
70  FORMAT(/3X,'Z',8X,'BD',9X,'W',7X,'T')
DO 80 I=1,M
WRITE(*,75)Z(I+1),BD(I),W(I),T(I)
WRITE(5,75)Z(I+1),BD(I),W(I),T(I)
75  FORMAT(F6.4,4X,F6.3,3X,F6.3,4X,F6.1)
80  CONTINUE
WRITE(*,85)
WRITE(5,85)
WRITE(*,90)B1,PAE,PDRAIN,SAND,SILT,CLAY,AT,BT,HT,XT,A1,A2,A3,A4
WRITE(5,90)B1,PAE,PDRAIN,SAND,SILT,CLAY,AT,BT,HT,XT,A1,A2,A3,A4
85  FORMAT(/'B1',3X,'PAE',2X,'PDRAIN',1X,'SAND',1X,'SILT',1X,'CLAY',
1  2X,'AT',2X,'BT',2X,'HT',2X,'XT',5X,'A1',6X,'A2',6X,'A3',5X,'A4')

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90  FORMAT(F3.1,1X,F4.1,1X,F4.1,2X,F4.2,1X,F4.2,1X,F4.2,2X,F4.2,
1  F4.2,F4.2,1X,F3.0,2X,E7.2,1X,E7.2,1X,E7.2,1X,E7.2)
C
C  COMPUTE CONSTANT AND VARIABLE SOIL PROPERTIES
C  *****
DO 150 I=1,M
  W(I)=W(I)*BD(I)
  WA(I)=W(I)
  VOL(I)=Z(I+2)-Z(I+1)
  MASS(I)=VOL(I)*BD(I)*1000.
  RESPIR(I)=SRESP*EXP(-Z(I+1)/0.05)*VOL(I)
  TA(I+1)=T(I)
  TN(I)=T(I)
  TA1(I)=T(I)
  POROS(I)=1.0-BD(I)/2.65
  FA(I)=POROS(I)-W(I)
  P(I)=PAE*(W(I)/POROS(I))*(-B1)
  PA(I+1)=P(I)
  PN(I)=P(I)
  AW(I)=EXP(MW*PA(I+1)/(R*TA(I+1)))
  VDS(I)=1.0D-3*EXP(31.3716-6014.79/TA(I+1)-7.9249D-3*TA(I+1))
1  /TA(I+1)
  S(I)=VDS(I)*(5307/TA(I+1)-1.0)/TA(I+1)
  DWV(I)=1.976D-5+1.4994D-7*TA(I+1)
  KSAT(I)=4.0D-6*(1.3/BD(I))*((1.3*B1)*EXP(-6.9*CLAY-3.7*SILT)
150  CONTINUE
  RNH3P=600.
  FCLOSE=.FALSE.
  MFLAG=0
C  *****
C  200  CALL SOILTW
C  *****
  MFLAG=MFLAG+1
  IF (MFLAG .GT. 1) GOTO 325

C  SET INITIAL CONCENTRATIONS
C  *****
DO 300 I=1,M
  PH(I)=IPH
  H(I)=10.0*(-PH(I))
  AH(I+1)=H(I)
  NH(I)=H(I)
  AOH(I+1)=KO(TA(I+1))/AH(I+1)
  NH4AQ(I)=1.0D-12
  ANH4AQ(I+1)=NH4AQ(I)
  NNH4AQ(I)=NH4AQ(I)
  NH4AD(I)=NK1*NH4AQ(I)*NK2
  ANH3AQ(I+1)=K2(TA(I+1))*ANH4AQ(I+1)/AH(I+1)
  NH3AQ(I)=ANH3AQ(I+1)
  NH3G(I+1)=ANH3AQ(I+1)/K1(TA(I+1))
  ACO2AQ(I+1)=K7(TA(I+1))*SCO2*EXP(-Z(I+1)/0.05)
  CO2AQ(I)=ACO2AQ(I+1)
  CO2G(I+1)=CO2AQ(I)/K7(TA(I+1))
  HCO3(I)=K8(TA(I+1))*ACO2AQ(I+1)/AH(I+1)
  AHCO3(I+1)=HCO3(I)
  NHC03(I)=HCO3(I)
  ACO3(I+1)=K9(TA(I+1))*AHCO3(I+1)/AH(I+1)
  CO3(I)=ACO3(I+1)
  N4HCO3(I)=NH4AQ(I)*HCO3(I)/K4(TA(I+1))

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```

NH4CO3(I)=NH4AQ(I)*CO3(I)/K5(TA(I+1))
CA(I)=0.5*HCO3(I)
CAAD(I)=(TCA*1.0D-6/40.)-(CA(I)*WA(I)/(BD(I)*1000.))
NCAAD(I)=CAAD(I)
NCA(I)=CA(I)
ACA(I+1)=CA(I)
CALC(I)=0.0
NCALC(I)=0.0
ACALC(I+1)=0.0
ADSH(I)=(A1*LOG(H(I))*3/(3.*LOG(10.))*3.)+A2*LOG(H(I))*2/(2.*
1 LOG(10.))*2.)+A3*LOG(H(I))/LOG(10.)+A4)*FSBC
HINIT=HINIT+H(I)*WA(I)+ADSH(I)*BD(I)*1000.
CAINIT=CAINIT+(CA(I)+CALC(I))*WA(I)+CAAD(I)*BD(I)*1000.
300 CONTINUE
NH3G(1)=NH3G(2)
CO2G(1)=1.2D-5
C *****
C CALL IVALUE
C *****
C CALL OUTPUT
C *****
325 GOTO 1115
IF (PERUH .LT. 99.99) THEN
C *****
C CALL UREA
C *****
ELSE
DO 350 I=1,M
350 U(I)=0.0
END IF
COUNT=0
FLAG=0
SUM=0.0
NSUM=0.0
RNH3=0.85*RNH3P+0.15*RA
IF (RNH3 .GT. 1000.) RNH3=1000.
C
C CARBON BALANCE FOR CARBONATE SPECIES
C *****
C LIQUID DIFFUSION EQUATION IS FROM CAMPBELL AND PAPENDICK (1980)
C GAS DIFFUSION EQUATION IS FROM SALLAM (1984)
C
375 DO 600 I=1,M
P14(I)=ANH4AQ(I+1)/K4(TA(I+1))
P11(I)=AH(I+1)/K8(TA(I+1))
P10(I)=P11(I)/K7(TA(I+1))
P12(I)=K9(TA(I+1))/AH(I+1)
P13(I)=P12(I)*ANH4AQ(I+1)/K5(TA(I+1))
CAP(I)=VOL(I)*(WA(I)*(P13(I)+P14(I)+P11(I)+P12(I)+1.0)+P10(I)*
1 FA(I))/DT
1 D(I+1)=2.8*(D13(TA(I+1))+P11(I)*D11(TA(I+1))+P12(I)*
1 D12(TA(I+1))+P13(I)*D8(TA(I+1))+P14(I)*D9(TA(I+1)))*
1 WA(I))*3.0+(P10(I)*D10(TA(I+1))*FA(I))*3.1/POROS(I)**2.)
600 CONTINUE
DO 700 I=1,N
D(I+1)=(D(I+1)+D(I+2))/(2.*(Z(I+2)-Z(I+1)))
700 CONTINUE
D(1)=0.0
D(M+1)=0.0

```

```

      AHC03(1)=AHC03(2)
      CO2LOS=(CO2G(2)-CO2G(1))/(1.267*RNH3/FRAC)
      IF (CO2LOS .LT. 0.0) CO2LOS=0.0
C     *****
      CALL CONVEC(AHC03)
C     *****
      DO 705 I=1,M
      JHC03(I)=JWC(I)
705  CONTINUE
C     *****
      CALL CONVEC(ACO2AQ)
C     *****
      DO 710 I=1,M
      JCO2AQ(I)=JWC(I)
710  CONTINUE
C     *****
      CALL CONVEC(ACO3)
C     *****
      DO 725 I=1,M
      A(I)=-FN*D(I)+4.*JA(I)
      B(I)=CAP(I)+FN*(D(I+1)+D(I))+4.*JB(I)
      C(I)=-FN*D(I+1)+4.*JC(I)
      F(I)=CAP(I)*(NHCO3(I)-HCO3(I))-D(I+1)*(AHC03(I+2)-AHC03(I+1))+
1      D(I)*(AHC03(I+1)-AHC03(I))-U(I)-RESPIR(I)+UCA(I)-JHC03(I)-
1      JCO2AQ(I)-JWC(I)
      IF (I .EQ. 1) F(I)=F(I)+CO2LOS
      NSUM=NSUM+ABS(F(I))
725  IF (ABS(F(I)) .LT. BTOLER) FLAG=FLAG+1
      CONTINUE
      SUM2=NSUM
      NSUM=0.0
      MINVAL=1.0D-5
      MAXVAL=0.1
C     *****
C     CALL SOLVE(NHCO3)
C     *****
      DO 750 I=1,M
      AHC03(I+1)=FN*NHCO3(I)+GN*HCO3(I)
      ACO2AQ(I+1)=AHC03(I+1)*AH(I+1)/K8(TA(I+1))
      CO2G(I+1)=ACO2AQ(I+1)/K7(TA(I+1))
      ACO3(I+1)=K9(TA(I+1))*AHC03(I+1)/AH(I+1)
750  CONTINUE
C
C     NITROGEN BALANCE FOR AMMONIACAL SPECIES
C     *****
      DO 400 I=1,M
      P5(I)=K2(TA(I+1))/AH(I+1)
      P4(I)=P5(I)/K1(TA(I+1))
      P9(I)=AHC03(I+1)/K4(TA(I+1))
      P8(I)=K9(TA(I+1))*AHC03(I+1)/(K5(TA(I+1))*AH(I+1))
      P6(I)=NK1*NK2*ANH4AQ(I+1)**(NK2-1.0)
      CAP(I)=VOL(I)*WA(I)*(P5(I)+P8(I)+P9(I)+1.0)+P4(I)*FA(I)+P6(I)*
1      BD(I)*1000.)/DT
      D(I+1) = 2.8*(D7(TA(I+1))+P5(I)*D5(TA(I+1))+P8(I)*D8(TA(I+1))+
1      +P9(I)*D9(TA(I+1)))*WA(I)**3.0+(P4(I)*D4(TA(I+1))*
1      FA(I))*3.1/POROS(I)**2.)
400  CONTINUE
      DO 500 I=1,N
      D(I+1)=(D(I+1)+D(I+2))/(2.*(Z(I+2)-Z(I+1)))

```

```

500  CONTINUE
      D(1)=0.0
      D(M+1)=0.0
      ANH4AQ(1)=ANH4AQ(2)
      NH3LOS=(NH3G(2)-NH3G(1))/RNH3
C    *****
      CALL CONVEC(ANH4AQ)
C    *****
      DO 505 I=1,M
        JNH4AQ(I)=JWC(I)
505  CONTINUE
C    *****
      CALL CONVEC(ANH3AQ)
C    *****
      DO 525 I=1,M
        A(I)=-FN*D(I)+2.*JA(I)
        B(I)=CAP(I)+FN*(D(I+1)+D(I))+2.*JB(I)
        C(I)=-FN*D(I+1)+2.*JC(I)
        F(I)=CAP(I)*(NNH4AQ(I)-NH4AQ(I))-D(I+1)*(ANH4AQ(I+2)-ANH4AQ(I+1))
1    +D(I)*(ANH4AQ(I+1)-ANH4AQ(I))-2.0*U(I)-JNH4AQ(I)-JWC(I)
        IF (I.EQ. 1) F(I)=F(I)+NH3LOS
        NSUM=NSUM+ABS(F(I))
        IF (ABS(F(I)) .LT. ATOLER) FLAG=FLAG+1
525  CONTINUE
      SUM1=NSUM
      NSUM=0.0
      MINVAL=0.0
      MAXVAL=0.01
C    *****
      CALL SOLVE(NNH4AQ)
C    *****
      DO 550 I=1,M
        ANH4AQ(I+1)=FN*NNH4AQ(I)+GN*NH4AQ(I)
        ANH3AQ(I+1)=K2(TA(I+1))*ANH4AQ(I+1)/AH(I+1)
        NH3G(I+1)=ANH3AQ(I+1)/K1(TA(I+1))
550  CONTINUE
C
C    CALCIUM MASS BALANCE
C    *****
      DO 775 I=1,M
        ADS(I)=P6(I)*(NNH4AQ(I)-NH4AQ(I))
        NCAAD(I)=CAAD(I)-0.5*ADS(I)
        UCAAD(I)=0.5*ADS(I)*MASS(I)/DT
        D(I+1)=2.8*D14(TA(I+1))*WA(I)*3.0
775  CONTINUE
      DO 800 I=1,N
        D(I+1)=(D(I+1)+D(I+2))/(2.*(Z(I+2)-Z(I+1)))
800  CONTINUE
      D(1)=0.0
      D(M+1)=0.0
C    *****
      CALL CONVEC(ACA)
C    *****
      DO 825 I=1,M
        CAP(I)=WA(I)*VOL(I)/DT
        A(I)=-FN*D(I)+2.*JA(I)
        B(I)=CAP(I)+FN*(D(I+1)+D(I))+2.*JB(I)
        C(I)=-FN*D(I+1)+2.*JC(I)

```

```

      F(I)=CAP(I)*(NCA(I)-CA(I))-D(I+1)*(ACA(I+2)-ACA(I+1))+D(I)*
1  (ACA(I+1)-ACA(I))+UCA(I)-UCAAD(I)-JCALC(I)-JWC(I)
      NSUM=NSUM+ABS(F(I))
      IF (ABS(F(I)) .LT. CTOLER) FLAG=FLAG+1
825  CONTINUE
      SUM3=NSUM
      NSUM=0.0
      MINVAL=0.0
      MAXVAL=0.1
C  *****
      CALL SOLVE(NCA)
C  *****
      DO 850 I=1,M
      ACA(I+1)=FN*NCA(I)+GN*CA(I)
850  CONTINUE
C
C  CHECK FOR CALCIUM CARBONATE PRECIPITATION OR DISSOLUTION
C  *****
      DO 900 I=1,M
      KC=K11(TA(I+1))
      CHECKC=ACA(I+1)*ACO3(I+1)
      G1=ACA(I+1)+ACO3(I+1)
      C1=ACA(I+1)*ACO3(I+1)-KC
      IF (CHECKC .GT. KC) THEN
      DELTA=WA(I)*VOL(I)*(G1-SQRT(G1*G1-4.*C1))/2.
      IF (DELTA .LT. 1.0D-37) DELTA=0.0
      UCA(I)=DELTA/DT
      NCALC(I)=CALC(I)+DELTA/(WA(I)*VOL(I))
      ACALC(I+1)=FN*NCALC(I)+GN*CALC(I)
      ELSE IF (CHECKC .LT. KC .AND. ACALC(I+1) .GT. 0.0) THEN
      DELTA=WA(I)*VOL(I)*(-G1+SQRT(G1*G1-4.*C1))/2.
      IF (DELTA/(WA(I)*VOL(I)) .GT. ACALC(I+1)) DELTA=ACALC(I+1)*
1  WA(I)*VOL(I)
      IF (DELTA .LT. 1.0D-37) DELTA=0.0
      UCA(I)=-DELTA/DT
      NCALC(I)=CALC(I)-DELTA/(WA(I)*VOL(I))
      ACALC(I+1)=FN*NCALC(I)+GN*CALC(I)
      END IF
900  CONTINUE
C
C  MASS BALANCE FOR HYDROGEN ION
C  *****
      DO 950 I=1,M
      BETA=(A1*PH(I)**2.0-A2*PH(I)+A3)*FSBC
      P1(I)=BETA/(LOG(10.)*AH(I+1))
      P2(I)=-KO(TA(I+1))/AH(I+1)**2.0
      D(I+1)=2.8*(D1(TA(I+1))-P2(I)*D2(TA(I+1)))*WA(I)**3.0
950  CONTINUE
      DO 960 I=1,N
      D(I+1)=(D(I+1)+D(I+2))/(2.*(Z(I+2)-Z(I+1)))
960  CONTINUE
      D(1)=0.0
      D(M+1)=0.0
C  *****
      CALL CONVEC(AH)
C  *****
      DO 970 I=1,M
      JH(I)=JWC(I)
970  CONTINUE

```

```

C      *****
C      CALL CONVEC(AOH)
C      *****
1      HCO2=K7(TA(2))* (1.+2.*P12(1))*CO2LOS*WA(1)/(FA(1)*
      (1.+2.*P11(1)+P12(1)))
      HNH3=K1(TA(2))*NH3LOS*WA(1)/(FA(1)*(1.+2.*P5(1)))
      DO 1000 I=1,M
      CAP(I)=(WA(I)*(1.+P2(I))+(BD(I)*1000.*P1(I)))*VOL(I)/DT
      A(I)=FN*D(I)
      B(I)=CAP(I)+FN*(D(I+1)+D(I))
      C(I)=FN*D(I+1)
      UHC(I)=(1.+4.*P11(I))*U(I)/(1.+2.*P11(I)+P12(I))
      UHN(I)=4.*P5(I)*U(I)/(1.+2.*P5(I))
      HCALC(I)=(1.+4.*P11(I))*UCA(I)/(1.+2.*P11(I)+P12(I))
      HRESP(I)=K7(TA(I+1))* (1.+2.*P12(I))*RESPIR(I)*WA(I)/(FA(I)*
1     (1.+2.*P11(I)+P12(1)))
      HADS(I)=2.*P5(I)*ADS(I)*WA(I)*VOL(I)/(DT*P6(I)*(1.+2.*P5(I)))
      HSINK(I)=UHC(I)+HADS(I)-UHN(I)-HCALC(I)-HRESP(I)
      F(I)=CAP(I)*(NH(I)-H(I))-D(I+1)*(AH(I+2)-AH(I+1))+D(I)*(AH(I+1)-
1     AH(I))+HSINK(I)-JH(I)+JWC(I)
      IF (I.EQ. 1) F(I)=F(I)+HCO2-HNH3
      NSUM=NSUM+ABS(F(I))
      IF (ABS(F(I)) .LT. HTOLER) FLAG=FLAG+1
1000  CONTINUE
      SUM4=NSUM
      NSUM=0.0
      MINVAL=1.0D-13
      MAXVAL=0.01
C      *****
C      CALL SOLVE(NH)
C      *****
      DO 1005 I=1,M
      AH(I+1)=FN*NH(I)+GN*H(I)
      PH(I)=-LOG10(AH(I+1))
      AOH(I+1)=KO(TA(I+1))/AH(I+1)
      NADSH(I)=ADSH(I)+P1(I)*(NH(I)-H(I))
1005  CONTINUE
C
C      CHECK FOR CONVERGENCE
C      *****
      IF (COUNT .GE. ITER) THEN
      WRITE(*,1050)COUNT,SUM1,SUM2,SUM3,SUM4,CO2LOS,NH3LOS
      WRITE(*,1055)UHC(1),UHN(1),HCALC(1),HADS(1),HRESP(1),HCO2,HNH3
      ELSE IF (FLAG .LT. 4*M) THEN
      FLAG=0
      COUNT=COUNT+1
      GOTO 375
      ELSE
      WRITE(*,1050)COUNT,SUM1,SUM2,SUM3,SUM4,CO2LOS,NH3LOS
      WRITE(*,1055)UHC(1),UHN(1),HCALC(1),HADS(1),HRESP(1),HCO2,HNH3
1050  FORMAT(13,' ',SUM1=',E7.2','SUM2=',E7.2','SUM3=',E7.2,
1     ' ',SUM4=',E7.2','CL=',E7.2','NL=',E7.2)
1055  FORMAT(' UC=',E7.2,' UN=',E7.2,' HOC=',E8.2,' HD=',E8.2,
1     ' RP=',E7.2,' HC=',E7.2,' HN=',E7.2)
      END IF
      FLAG=90
      COUNT=0

```

```

C      UPDATE ALL VALUES
C      *****
C      DO 1100 I=1,M
      NH3AQ(I)=K2(TA(I+1))*NNH4AQ(I)/NH(I)
      ANH3AQ(I+1)=NH3AQ(I)
      CO2AQ(I)=NHCO3(I)*NH(I)/K8(TA(I+1))
      ACO2AQ(I+1)=CO2AQ(I)
      NH3G(I+1)=NH3AQ(I)/K1(TA(I+1))
      CO2G(I+1)=CO2AQ(I)/K7(TA(I+1))
      CO3(I)=K9(TA(I+1))*NHCO3(I)/NH(I)
      ACO3(I+1)=CO3(I)
      N4HCO3(I)=NNH4AQ(I)*NHCO3(I)/K4(TA(I+1))
      NH4CO3(I)=NNH4AQ(I)*CO3(I)/K5(TA(I+1))
      NH4AD(I)=NH4AD(I)+ADS(I)
      NH4AQ(I)=NNH4AQ(I)
      ANH4AQ(I+1)=NNH4AQ(I)
      HCO3(I)=NHCO3(I)
      AHCO3(I+1)=NHCO3(I)
      H(I)=NH(I)
      AH(I+1)=NH(I)
      PH(I)=-LOG10(NH(I))
      AOH(I+1)=K0(TA(I+1))/NH(I)
      CA(I)=NCA(I)
      ACA(I+1)=NCA(I)
      CAAD(I)=NCAAD(I)
      CALC(I)=NCALC(I)
      ACALC(I+1)=NCALC(I)
      ADSH(I)=NADSH(I)
      HGEN=HGEN-HSINK(I)*DT/VOL(I)
1100  CONTINUE
      HGEN=HGEN+(HNH3-HCO2)*DT/VOL(1)
      TLOSS=TLOSS+NH3LOS*DT
      LOSS=0.5*TLOSS/TOTALU
C      *****
C      CALL DVALUE
C      *****
C      CALL IVALUE
C      *****
      WRITE(*,1060)DHCO3(1),DCO2AQ(1),DCO2G(1),DNH4AQ(1),DNH3AQ(1),
1    DNH3G(1)
1060  FORMAT(' DC3=',E8.2,' DC2=',E8.2,' DOG=',E8.2,' DN4=',E8.2,
1    ' DN3=',E8.2,' DNG=',E8.2)
1105  IF (HOUR.EQ. 0.AND. MIN.EQ. 0.OR. HOUR.EQ. 6.AND. MIN.EQ.
1    0.OR. HOUR.EQ. 12.AND. MIN.EQ. 0.OR. HOUR.EQ. 18.AND. MIN
1    .EQ. 0) CALL OUTPUT
1115  WRITE(*,1120)DAY,HOUR,MIN,PH(1),WA(1),TA(2)-273.15,PERUH,
1    LOSS*100.,NYIELD,CYIELD,NRECOV,CRECOV,SHYD
1120  FORMAT(I4,2I3,1X,F5.2,1X,F5.2,1X,F5.4,1X,F6.2,1X,F6.2,1X,E9.4,1X,F6.2,
1    1X,F6.2,1X,F6.2,1X,F6.2,1X,F5.1)
      DAY=0
      HOUR=0
      MIN=0
C      *****
C      CALL UPDATE
C      *****
      IF (FCLOSE) GOTO 1130
      GOTO 200
1130  END

```

```

C      SUBROUTINE SOILTW
C      *****
      IMPLICIT REAL*8 (A-Z)
      INTEGER*2 I,J,L,M,N,JJ, DAY, HOUR, MIN, DT, FLAG, NFLAG, COUNT, REALT(3)
      LOGICAL*2 FCLOSE
      PARAMETER (L=50, R=8.314, SBCST=5.67E-8, GR=9.81, DW=1.0D3)
      DIMENSION RELW(L)
      COMMON /BLKO/U(L), ANH4AQ(L), AUAQ(L), PERUH, LOSS, HYD, SHYD
1      /BLK1/Z(L), VOL(L), P(L), FA(L), POROS(L), CAP(L), D(L), TOTALU
1      /BLK3/A(L), B(L), C(L), F(L), MAXVAL, MINVAL, NFLAG
1      /BLK7/TAIR, VDA, UHM, RA, RH, PCP, PA(L), PN(L), AW(L), VDS(L), S(L),
1      DWV(L), WAP(L), TA1(L), RNH3P, RNH3, JA(L), JB(L), JC(L)
1      /BLK8/T(L), TA(L), TN(L), W(L), WA(L), BD(L), TSURF, HOUR, DAY, MIN
1      /BLK9/MW, LHV, PAE, B1, SAND, SILT, CLAY, KSAT(L), B2, AT, BT, HT,
1      XT, CT, PDRAIN, KVP(L), KVT(L), KW(L), KH(L), EVAP, RAIN,
1      PRECIP, JW(L), JWC(L), ERR(L), FH, FU, FW, FO, GH, GU, GW, GO
1      /BLK10/M, N, JJ, OCARB, DT, TDEPTH

C      READ METEOREOLOGICAL DATA
C      *****
      READ(2,*,END=9000)(REALT(J), J=1,3), UHM, TSURF, TAIR, T6CM, T15CM,
1      T30CM, SW, RSW, VDA, CLDCOV, RAIN
      WRITE(*,5)UHM, TSURF-273.15, TAIR-273.15, T6CM-273.15, T15CM-273.15,
1      T30CM-273.15, SW, RSW, VDA, CLDCOV, RAIN
5      FORMAT(/F4.2,5F6.2,2F7.2,F8.5,2F6.2)
      IF (RAIN .GT. 0.0) PRECIP=RAIN/1.0D3
      IF (PRECIP .LE. 0.0) GOTO 1400
      DO 1300 I=1,M
        W(I)=W(I)+PRECIP/VOL(I)
        P(I)=PAE*(W(I)/POROS(I))*(-B1)
        PRECIP=0.0
1300    CONTINUE
      DO 1350 I=1,N
        PN(I)=P(I)
        PA(I+1)=PN(I)
        WA(I)=W(I)
        FA(I)=POROS(I)-WA(I)
        AW(I)=EXP(MW*PA(I+1)/(R*TA(I+1)))
1350    CONTINUE
1400    IF (DAY .EQ. 0 .AND. HOUR .EQ. 0 .AND. MIN .EQ. 0) THEN
      DAY=REALT(1)
      HOUR=REALT(2)
      MIN=REALT(3)
      END IF
      IF (TDEPTH .GE. 0.2 .AND. TDEPTH .LE. 0.3) THEN
        T(M)=T30CM
      ELSE IF (TDEPTH .GE. 0.1 .AND. TDEPTH .LE. 0.19) THEN
        T(M)=T15CM
      ELSE IF (TDEPTH .GE. 0.06 .AND. TDEPTH .LE. 0.09) THEN
        T(M)=T6CM
      END IF
      TN(M)=T(M)
      TA(JJ)=T(M)
      EA=1.56*VDA**0.143
      EA=(1.0-0.84*CLDCOV)*EA+0.84*CLDCOV
      COUNT=0
      FLAG=0

```

```

C *****
1450 CALL RESIST(TA(2))
C *****
EVAP=(VDS(1)*AW(1)-VDA)/(RA*DW)
DO 1500 I=1,M
RELW(I)=WA(I)/POROS(I)
ETA1=9.5+3.0*RELW(I)
IF (RELW(I) .GT. 0.5) THEN
ETA2=0.0
ELSE
ETA2=8.5*EXP(-(3.5*RELW(I))*4.0)
END IF
ETA=ETA1-ETA2
KPV=DWV(I)*FA(I)**3.1/POROS(I)**2.0*VDS(I)*AW(I)*MW/(R*TA(I+1))
KTV=DWV(I)*FA(I)**3.1/POROS(I)**2.0*AW(I)*S(I)*ETA
IF (I .NE. 1) THEN
KVP(I)=1.0D-3*SQR(KP*KPV)/(Z(I+1)-Z(I))
KVT(I)=1.0D-3*SQR(KT*KTV)/(Z(I+1)-Z(I))
END IF
KP=KPV
KT=KTV
1500 CONTINUE

C
C SOLVE FOR SOIL TEMPERATURE
C *****
ES=0.9+0.18*WA(1)
ALBEDO=0.24-0.59*WA(1)/BD(1)
DO 1550 I=1,M
KHC1=AT+BT*RELW(I)
IF (RELW(I) .GT. 0.15) THEN
KHC2=0.0
ELSE
KHC2=(AT-BT)*EXP(-(CT*RELW(I))*XT)
END IF
KHC=KHC1-KHC2
IF (I .NE. 1) KH(I)=SQRT(KHT*KHC)/(Z(I+1)-Z(I))+LHV*KVT(I)
KHT=KHC
1550 CONTINUE
DO 1600 I=1,N
U(I)=LHV*(KVP(I+1)*(PA(I+2)-PA(I+1))-KVP(I)*(PA(I+1)-PA(I)))
1600 CONTINUE
U(1)=U(1)+SW*(1.0-ALBEDO)+EA*ES*SBCST*TAIR**4-ES*SBCST*
1 TA(2)**4 -EVAP*LHV*DW-PCP*(TA(2)-TAIR)/RH
DO 1650 I=1,N
CAP(I)=(2.4D6*BD(I))/2.65+4.18D6*WA(I))*VOL(I)/DT
A(I)=-FH*KH(I)
B(I)=CAP(I)+FH*(KH(I+1)+KH(I))
C(I)=-FH*KH(I+1)
F(I)=CAP(I)*(TN(I)-T(I))-KH(I+1)*(TA(I+2)-TA(I+1))+KH(I)*(TA(I+1)
1 -TA(I))-U(I)
TERR=TERR+ABS(F(I))
1650 CONTINUE
ERRH=TERR
IF (TERR .LT. 3.0) FLAG=FLAG+1
TERR=0.0
MAXVAL=373.15
MINVAL=273.15
NFLAG=1

```

```

C *****
C CALL SOLVE(TN)
C *****
C
C SOLVE FOR SOIL WATER POTENTIAL AND SOIL WATER FLUX
C *****
DO 1700 I=1,N
  U(I)=KVT(I+1)*(TA(I+2)-TA(I+1))-KVT(I)*(TA(I+1)-TA(I))
  KW(I+1)=KSAT(I)*SQRT((PAE/PA(I+1))*B2*(PAE/PA(I+2))*B2)/
1 (Z(I+2)-Z(I+1))+KVP(I+1)
  JW(I+1)=-KW(I+1)*(PA(I+2)-PA(I+1)-GR*(Z(I+2)-Z(I+1)))-KVT(I+1)*
1 (TA(I+2)-TA(I+1))
1700 CONTINUE
  U(1)=U(1)-EVAP
  SFLUX=JW(2)
  IF (JW(2) .LT. 0.0) JW(2)=0.0
  DO 1750 I=1,N
    CAP(I)=-WA(I)*VOL(I)/(B1*PA(I+1)*DT)
    A(I)=-FW*KW(I)
    B(I)=CAP(I)+FW*(KW(I+1)+KW(I))
    C(I)=-FW*KW(I+1)
    F(I)=CAP(I)*(PN(I)-P(I))-KW(I+1)*(PA(I+2)-PA(I+1))+KW(I)*(PA(I+1)
1 -PA(I))+GR*(Z(I+2)-Z(I+1))*KW(I+1)-GR*(Z(I+1)-Z(I))*KW(I)-U(I)
    WERR=WERR+ABS(F(I))
1750 CONTINUE
    ERRW=WERR
    IF (WERR .LT. 3.0D-10) FLAG=FLAG+1
    WERR=0.0
    MAXVAL=PAE
    MINVAL=-1.0D6
    NFLAG=1
C *****
C CALL SOLVE(PN)
C *****
C
C CALCULATE AVERAGE VALUES
C *****
DO 1800 I=1,N
  TA1(I)=FO*(FH*TN(I)+GH*T(I))+GO*TA1(I)
  TA(I+1)=TA1(I)
  PA(I+1)=FW*PN(I)+GW*P(I)
  WA(I)=POROS(I)*((PN(I)/PAE)*(-1.0/B1)+(P(I)/PAE)*(-1.0/B1))/2.0
  FA(I)=POROS(I)-WA(I)
  VDS(I)=1.0D-3*EXP(31.3716-6014.79/TA(I+1)-7.9249D-3*TA(I+1))/
1 TA(I+1)
  S(I)=VDS(I)*(5307./TA(I+1)-1.0)/TA(I+1)
  DWV(I)=-1.9760D-5+1.4994D-7*TA(I+1)
  AW(I)=EXP(MW*PA(I+1)/(R*TA(I+1)))
1800 CONTINUE
  P(M)=P(N)
  PA(JJ)=PA(M)
  PN(M)=PN(N)
  IF (COUNT .GE. 50) THEN
    WRITE(*,1810)ERRH,ERRW
    WRITE(5,1810)ERRH,ERRW
1810 FORMAT(' No convergence: ERRH=',E9.4,', ERRW=',E9.4)
  ELSE IF (FLAG .LT. 2) THEN
    FLAG=0
    COUNT=COUNT+1

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GOTO 1450
ELSE
WRITE(*,1820)COUNT,ERRH,ERRW,RA,RH,FA(1)
1820 FORMAT(' COUNT=',I3,' , ERRH=',ES.3,' , ERRW=',ES.3,' , RA=',
1 F7.0,' , RH=',F7.0,' , FA=',F6.3)
WRITE(*,1830)SFLUX,JW(3),JW(4),JW(5),JW(6)
1830 FORMAT(' JW(2)='ES.2,' , JW(3)='ES.2,' , JW(4)='ES.2,' , JW(5)='
1 ES.2,' , JW(6)='ES.2)
END IF
IF (REALT(2) .EQ. 0 .AND. REALT(3) .EQ. 0 .OR. REALT(2) .EQ. 6
1 .AND. REALT(3) .EQ. 0 .OR. REALT(2) .EQ. 12 .AND. REALT(3) .EQ.
10 .OR. REALT(2) .EQ. 18 .AND. REALT(3) .EQ. 0) THEN
WRITE(5,20)
WRITE(5,10)UHM,TSURF-273.15,TAIR-273.15,T6CM-273.15,T15CM-273.15,
1 T30CM-273.15,SW,RSW,VDA,CLDCOV,RAIN,RA,RH
10 FORMAT(F4.2,F6.1,1X,F6.1,2F6.1,1X,F6.1,2F5.1,F8.5,1X,F4.2,3X,
1F4.2,2X,F7.0,F5.0)
20 FORMAT('////' UHM',2X,'TSURF',2X,'TAIR',2X,'T6CM',2X,'T15CM',2X,
1'T30CM',2X,'SW',2X,'RESW',3X,'VDA',2X,'CLDCOV',2X,'RAIN',3X,'RA',
1 5X,'RH')
END IF
COUNT=0
FLAG=0
GOTO 9001
9000 FCLOSE=.TRUE.
9001 RETURN
END

C
SUBROUTINE UPDATE
C
*****
IMPLICIT REAL*8 (A-Z)
INTEGER*2 I,J,L,M,N,JJ,DT,ITER,DAY,HOUR,MIN
PARAMETER (L=50,R=8,314)
COMMON /BLK1/Z(L),VOL(L),P(L),FA(L),POROS(L),CAP(L),D(L),TOTALU
1 /BLK7/TAIR,VDA,UHM,RA,RH,PCP,PA(L),PN(L),AW(L),VDS(L),S(L),
1 DWV(L),WAP(L),TA1(L),RNH3P,RNH3,JA(L),JB(L),JC(L)
1 /BLK8/T(L),TA(L),TN(L),W(L),WA(L),BD(L),TSURF,HOUR,DAY,MIN
1 /BLK9/MW,LHV,PAE,B1,SAND,SILT,CLAY,KSAT(L),B2,AT,BT,HT,
1 XT,CT,PDRAIN,KVP(L),KVT(L),KW(L),KH(L),EVAP,RAIN,
1 PRECIP,JW(L),JWC(L),ERR(L),FH,FU,FW,FO,GH,GU,GW,GO
1 /BLK10/M,N,JJ,OCARB,DT,TDEPTH

C
DO 1850 I=1,M
T(I)=TN(I)
TA(I+1)=TN(I)
TA1(I)=TN(I)
P(I)=PN(I)
PA(I+1)=PN(I)
W(I)=POROS(I)*(PN(I)/PAE)**(-1.0/B1)
WA(I)=W(I)
FA(I)=POROS(I)-WA(I)
VDS(I)=1.0D-3*EXP(31.3716-6014.79/TA(I+1)-7.9249D-3*TA(I+1))/
1 TA(I+1)
S(I)=VDS(I)*(5307./TA(I+1)-1.0)/TA(I+1)
DWV(I)=-1.9760D-5+1.4994D-7*TA(I+1)
AW(I)=EXP(MW*PA(I+1)/(R*TA(I+1)))
1850 CONTINUE
P(M)=P(N)
PN(M)=PN(N)

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PA(JJ)=PA(M)
RNH3P=RNH3
RETURN
END

C
SUBROUTINE RESIST(TSOIL)
*****
IMPLICIT REAL*8 (A-Z)
INTEGER*2 I,L,M,N,JJ,DT,COUNT,DAY,HOUR,MIN
PARAMETER (L=50,KVON=.35,R=8.314,GR=9.81,MA=.02897)
COMMON /BLK7/TAIR,VDA,UHM,RA,RH,PCP,PA(L),PN(L),AW(L),VDS(L),S(L),
1 DWV(L),WAP(L),TA1(L),RNH3P,RNH3,JA(L),JB(L),JC(L)
1 /BLKS/T(L),TA(L),TN(L),W(L),WA(L),BD(L),TSURF,HOUR,DAY,MIN
1 /BLK9/MW,LHV,PAE,B1,SAND,SILT,CLAY,KSAT(L),B2,AT,BT,HT,
1 XT,CT,PDRAIN,KVP(L),KVT(L),KW(L),KH(L),EVAP,RAIN,
1 PRECIP,JW(L),JWC(L),ERR(L),FH,FU,FW,FO,GH,GU,GW,GO
1 /BLK10/M,N,JJ,OCARB,DT,TDEPTH

C
COUNT=0
TP=101.0D3
ZO=.005
HM=1.6
LN=LOG(HM/ZO)
THETA=SQRT(TAIR*TSOIL)
IF (TAIR.GT. TSOIL) THETA=TAIR-THETA+TSOIL
VP=(VDA*R*THETA)/MW
DA=((TP-VP)*MA)/(R*THETA)
PCP=VDA*1.87D3+DA*1.005D3
RH=100.0
ZETA=0.0
1900 SHF=PCP*(TSOIL-TAIR)/RH
IF (ZETA.GE. 0.0) GOTO 2000
XC=(1.0-15.0*ZETA)**(0.25)
FC=2.0*LOG((1.0+XC)/2.0)+LOG((1+XC*XC)/2.0)
1 -2.0*ATAN(XC+1.5708)
USTAR=KVON*UHM/(LN-FC)
GOTO 2150
2000 USTAR=KVON*UHM/(LN+4.7*ZETA)
2150 ZETA=-KVON*GR*SHF/HM/(PCP*THETA*USTAR**3)
IF (ZETA.GE. 20.0) ZETA=20.0
IF (ZETA.GE. 0.0) GOTO 2200
Y=(1.0-9.0*ZETA)**(0.5)
RH=0.74*(LN-LOG((1.0+Y)/2.0))/(KVON*USTAR)
XC=(1.0-15.0*ZETA)**(0.25)
FC=2.0*LOG((1.0+XC)/2.0)+LOG((1.0+XC*XC)/2.0)-2*ATAN(XC+1.5708)
RA=(LN-FC)/(KVON*USTAR)
GOTO 2250
2200 RH=(0.74*LN+4.7*ZETA)/(KVON*USTAR)
RA=(LN+4.7*ZETA)/(KVON*USTAR)
2250 IF (RH.GT. 1000.) RH=1000.
IF (RH.LE. 0.) RH=1.
IF (COUNT.GE. 100) THEN
WRITE(*,2260)
WRITE(5,2260)
2260 FORMAT(' No convergence in RESIST')
COUNT=0
ELSE IF (ABS((RH-RHOLD)/RH).GE. 5.0D-3 .OR.
1 ABS((RA-RAOLD)/RA).GE. 5.0D-3) THEN
COUNT=COUNT+1

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RHOLD=RH
RAOLD=RA
GOTO 1900
ELSE
COUNT=0
END IF
RETURN
END

C
SUBROUTINE UREA
C *****
IMPLICIT REAL*8 (A-Z)
INTEGER*2 I, J, L, M, N, JJ, FLAG, NFLAG, START, COUNT, DT, DAY, HOUR, MIN
PARAMETER (L=50)
DIMENSION USOLID(L), UAQ(L), NUAQ(L), ERRU(L)
COMMON /BLK0/U(L), ANH4AQ(L), AUAQ(L), PERUH, LOSS, HYD, SHYD
1 /BLK1/Z(L), VOL(L), P(L), FA(L), POROS(L), CAP(L), D(L), TOTALU
1 /BLK2/PH(L), MASS(L), FLAG, RESPIR(L)
1 /BLK3/A(L), B(L), C(L), F(L), MAXVAL, MINVAL, NFLAG
1 /BLK7/TAIR, VDA, UHM, RA, RH, PCP, PA(L), PN(L), AW(L), VDS(L), S(L),
1 DWV(L), WAP(L), TAI(L), RNH3P, RNH3, JA(L), JB(L), JC(L)
1 /BLK8/T(L), TA(L), TN(L), W(L), WA(L), BD(L), TSURF, HOUR, DAY, MIN
1 /BLK9/MW, LHV, PAE, B1, SAND, SILT, CLAY, KSAT(L), B2, AT, BT, HT,
1 XT, CT, PDRAIN, KVP(L), KVT(L), KW(L), KH(L), EVAP, RAIN,
1 PRECIP, JW(L), JWC(L), ERR(L), FH, FU, FW, FO, GH, GU, GW, GO
1 /BLK10/M, N, JJ, OCARB, DT, TDEPTH

C
IF (START .EQ. 0) THEN
START=1
USOLID(1)=TOTALU
END IF
MAXVAL=0.0
INITIALIZE AND ADJUST UREA CONCENTRATION
C *****
C
DO 2350 I=1, M
IF (FLAG .EQ. 90) THEN
UAQ(I)=NUAQ(I)*WAP(I)/WA(I)
AUAQ(I+1)=NUAQ(I)*WAP(I)/WA(I)
END IF
USAT=-1258.9+13.2843*TA(I+1)-0.047381*TA(I+1)**2.0
1 +5.77264D-5*TA(I+1)**3.0
USAT=USAT/(1+USAT*0.0453)
IF (USAT .GT. MAXVAL) MAXVAL=USAT
IF (UAQ(I) .GT. USAT) THEN
USOLID(I)=USOLID(I)+(UAQ(I)-USAT)*WA(I)*VOL(I)
UAQ(I)=USAT
ELSE IF (USOLID(I) .EQ. 0.0) THEN
GOTO 2300
ELSE IF (UAQ(I) .LT. USAT .AND. USOLID(I) .GT. (USAT-UAQ(I))
1 *WA(I)*VOL(I)) THEN
USOLID(I)=USOLID(I)-(USAT-UAQ(I))*WA(I)*VOL(I)
UAQ(I)=USAT
ELSE IF (UAQ(I) .LT. USAT .AND. USOLID(I) .LE. (USAT-UAQ(I))
1 *WA(I)*VOL(I)) THEN
UAQ(I)=UAQ(I)+USOLID(I)/(WA(I)*VOL(I))
USOLID(I)=0.0
2300 END IF
IF (FLAG .EQ. 90) THEN
NUAQ(I)=UAQ(I)

```

```

      AUAQ(I+1)=NUAQ(I)
      END IF
2350  CONTINUE
C
C      COMPUTE DIFFUSIVITY OF UREA
C      *****
      DO 2400 I=1,M
      DU=-1.269D-8+4.957D-11*TA(I+1)
      D(I+1)=2.8*DU*WA(I)**3.0
2400  CONTINUE
      DO 2425 I=1,N
      D(I+1)=(D(I+1)+D(I+2))/(2.*(Z(I+2)-Z(I+1)))
2425  CONTINUE
      FLAG=0
      COUNT=0
C      *****
2450  CALL HYDROL
C      *****
      D(1)=0.0
      D(M+1)=0.0
C      *****
      CALL CONVEC(AUAQ)
C      *****
      DO 2500 I=1,M
      CAP(I)=WA(I)*VOL(I)/DT
      A(I)=-FU*D(I)+JA(I)
      B(I)=CAP(I)+FU*(D(I+1)+D(I))+JB(I)
      C(I)=-FU*D(I+1)+JC(I)
      F(I)=CAP(I)*(NUAQ(I)-UAQ(I))-D(I+1)*(AUAQ(I+2)-AUAQ(I+1))
      +D(I)*(AUAQ(I+1)-AUAQ(I))+U(I)-JWC(I)
1      ERR(I)=ABS(F(I))
      NSUM=NSUM+ERR(I)
2500  CONTINUE
      UERR=ABS((NSUM-SUM)/NSUM)
      IF (UERR .LT. 0.01) FLAG=FLAG+1
      SUM=NSUM
      NSUM=0.0
      MINVAL=0.0
C      *****
      CALL SOLVE(NUAQ)
C      *****
      DO 2550 I=1,M
      AUAQ(I+1)=FU*NUAQ(I)+GU*UAQ(I)
2550  CONTINUE
      IF (COUNT .GE. 50) THEN
      WRITE(*,2560)UERR,ERR(1),ERR(2),ERR(3)
      WRITE(5,2560)UERR,ERR(1),ERR(2),ERR(3)
2560  FORMAT(' No convergence: UERR =',E9.4,' , F(1) =',E9.4,
1      ' , F(2) =',E9.4,' , F(3) =',E9.4)
      ELSE IF (FLAG .LT. 1) THEN
      COUNT=COUNT+1
      FLAG=0
      GOTO 2450
      ELSE
      WRITE(*,2580)COUNT,UERR,ERR(1),ERR(2),ERR(3),ERR(4)
2580  FORMAT(' COUNT=',I2,' , UERR=',E8.2,' , F(1) =',E8.2,' , F(2) =',E8.2,
1      ' , F(3) =',E8.2,' , F(4) =',E8.2)
      END IF
      COUNT=0

```

```

FLAG=0
DO 2600 I=1,M
HYD=HYD+U(I)*DT
THYD=THYD+U(I)
2600 CONTINUE
PERUH=100.*HYD/TOTALU
SHYD=100.*U(1)/THYD
THYD=0.0
RETURN
END

C
SUBROUTINE HYDROL
C *****
IMPLICIT REAL*8 (A-Z)
INTEGER*2 I,L,M,N,JJ,DT,FLAG,DAY,HOUR,MIN
PARAMETER (L=50)
COMMON /BLK0/U(L),ANH4AQ(L),AUAQ(L),PERUH,LOSS,HYD,SHYD
1 /BLK1/Z(L),VOL(L),P(L),FA(L),POROS(L),CAP(L),D(L),TOTALU
1 /BLK2/PH(L),MASS(L),FLAG,RESPIR(L)
1 /BLK7/TAIR,VDA,UHM,RA,RH,PCP,PA(L),PN(L),AW(L),VDS(L),S(L),
1 DWV(L),WAP(L),TA1(L),RNH3P,RNH3,JA(L),JB(L),JC(L)
1 /BLK8/T(L),TA(L),TN(L),W(L),WA(L),BD(L),TSURF,HOUR,DAY,MIN
1 /BLK10/M,N,JJ,OCARB,DT,TDEPTH

C
MWU=60.06
KM=3.34D-3
AE=5.4D4
M310=(4.259D-9*OCARB+1.4079D-9)/MWU
VM=M310/EXP(-AE/(8.314*M310.))
DO 2700 I=1,M
VMAX=VM*EXP(-AE/(8.314*TA(I+1)))
IF (PA(I+1).LT. -8.3D4) THEN
PEFF=0.0105
ELSE IF (PA(I+1).GE. -8.3D4 .AND. PA(I+1).LE. -1.0) THEN
PEFF=0.745764+0.393878*(LOG10(-PA(I+1)))-0.205175*
1 (LOG10(-PA(I+1)))**2.0 + 0.037422*(LOG10(-PA(I+1)))**3.0 -
1 0.00370941*(LOG10(-PA(I+1)))**4.0
ELSE
PEFF=0.75
END IF
PHEFF=EXP(-0.064*(PH(I)-6.5)**2)
CEFF=1.0
V=VMAX*PEFF*PHEFF*CEFF*AUAQ(I+1)/(KM+AUAQ(I+1))
U(I)=V*MASS(I)
2700 CONTINUE
RETURN
END

C
SUBROUTINE SOLVE(NEWVAL)
C *****
IMPLICIT REAL*8 (A-Z)
INTEGER*2 I,L,M,N,JJ,DT,NFLAG,DAY,HOUR,MIN
PARAMETER (L=50)
DIMENSION NEWVAL(L)
COMMON /BLK3/A(L),B(L),C(L),F(L),MAXVAL,MINVAL,NFLAG
1 /BLK8/T(L),TA(L),TN(L),W(L),WA(L),BD(L),TSURF,HOUR,DAY,MIN
1 /BLK10/M,N,JJ,OCARB,DT,TDEPTH

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```

C
  COEFF=1.0
  IF (NFLAG .EQ. 1) THEN
    M=M-1
    COEFF=0.25
    END IF
    DO 2750 I=1,M-1
      C(I)=C(I)/B(I)
      F(I)=F(I)/B(I)
      B(I+1)=B(I+1)-A(I+1)*C(I)
      F(I+1)=F(I+1)-A(I+1)*F(I)
2750 CONTINUE
      DVAL=COEFF*F(M)/B(M)
      NEWVAL(M)=NEWVAL(M)-DVAL
      IF (NEWVAL(M) .GT. MAXVAL) NEWVAL(M)=MAXVAL
      IF (NEWVAL(M) .LT. MINVAL) NEWVAL(M)=MINVAL

C
C  BACK SUBSTITUTION
  DO 2775 I=M-1,1,-1
    DVAL=COEFF*F(I)-C(I)*DVAL
    NEWVAL(I)=NEWVAL(I)-DVAL
    IF (NEWVAL(I) .GT. MAXVAL) NEWVAL(I)=MAXVAL
    IF (NEWVAL(I) .LT. MINVAL) NEWVAL(I)=MINVAL
2775 CONTINUE
    IF (NFLAG .EQ. 1) THEN
      M=M+1
      NFLAG=NFLAG-1
    END IF
    RETURN
  END

C
C  SUBROUTINE IVALUE
  *****
  IMPLICIT REAL*8 (A-Z)
  INTEGER*2 I,L,M,N,JJ,DT,DAY,HOUR,MIN
  PARAMETER (L=50)
  COMMON /BLK1/Z(L),VOL(L),P(L),FA(L),POROS(L),CAP(L),D(L),TOTALU
1 /BLK5/NH4AQ(L),NH3AQ(L),HCO3(L),CO2AQ(L),H(L),MU(L),CA(L)
1 /BLK7/TAIR,VDA,UHM,RA,RH,PCP,PA(L),PN(L),AW(L),VDS(L),S(L),
1 DWV(L),WAP(L),TA1(L),RNH3P,RNH3,JA(L),JB(L),JC(L)
1 /BLK8/TA(L),TA(L),TN(L),W(L),WA(L),BD(L),TSURF,HOUR,DAY,MIN
1 /BLK10/M,N,JJ,OCARB,DT,TDEPTH
1 /BLK11/NH4AD(L),NH4CO3(L),N4HCO3(L),NH3G(L),NH3LOS,CO2LOS
1 /BLK12/INH4AQ(L),INH3AQ(L),INH4AD(L),INH3G(L),INH4C3(L),IH(L),
1 IN4HC3(L),ICO2AQ(L),IHC03(L),ICO3(L),ICO2G(L),ICALC(L)
1 /BLK13/CO3(L),CO2G(L),CALC(L),NYIELD,CYIELD,NRECOV,CRECOV,HGEN
1 /BLK14/ADSH(L),HINIT,CAINIT,DNH4AQ(L),DHCO3(L),DNH3AQ(L),
1 DCO2AQ(L),DCO2G(L),DNH3G(L),CAACT,HACT,IADSH(L),CAAD(L)

C
  DO 10 I=1,M
    INH4AQ(I)= NH4AQ(I)*WA(I)
    INH3AQ(I)= NH3AQ(I)*WA(I)
    INH4AD(I)= NH4AD(I)
    INH3G(I)= NH3G(I+1)*FA(I)
    INH4C3(I)= NH4CO3(I)*WA(I)
    IN4HC3(I)= N4HCO3(I)*WA(I)
    ICO2AQ(I)= CO2AQ(I)*WA(I)
    IHC03(I)= HCO3(I)*WA(I)
    ICO3(I)= CO3(I)*WA(I)

```



```

NACCT = NH3LOS*DT + DTN
NYIELD = 100.*NACCT/NHYD
15 CHYD = UHYD
CACCT = CO2LOS*DT + DTC
CYIELD = 100.*CACCT/(CHYD+CO2RES)
RESP = RESP + CO2RES
NLOS = NLOS + NH3LOS*DT
CLOS = CLOS + CO2LOS*DT
DNT = DNT + DTN
DCT = DCT + DTC
UNHYD = TOTALU - HYD
NBAL = 2.*UNHYD + NLOS + DNT
CBAL = UNHYD + CLOS + DCT
NRECOV = 100.*NBAL/(2.0*TOTALU)
CRECOV = 100.*CBAL/(TOTALU+RESP)
HACT = 100.*(HNEW+HADSNU-HGEN)/HINIT
CAACT = 100.*(CANEW+CLCNEW+CAADNU)/CAINIT
WRITE(*,20)RESP,CLOS,HACT,CAACT,TDH,TDHADS,DH
20 FORMAT(' RP=',E7.2,' C2=',E7.2,' %H=',F5.1,' %CA=',F5.1,
1 ' ,TH=',E8.2,' AD=',E8.2,' DH=',E8.2)

C
C
C
SET TIME STEP SUMMATION TERMS TO ZERO
*****
DTC=0.0
DTN=0.0
UHYD=0.0
CO2RES=0.0
CANEW=0.0
CLCNEW=0.0
CAADNU=0.0
HNEW=0.0
HADSNU=0.0
DH=0.0
RETURN
END

C
C
SUBROUTINE CONVEC(CONC)
*****
IMPLICIT REAL*8 (A-Z)
INTEGER*2 I,L,M,N,JJ,DT
PARAMETER (L=50)
DIMENSION CONC(L)
COMMON /BLK0/U(L),ANH4AQ(L),AUAQ(L),PERUH,LOSS,HYD,SHYD
1 /BLK7/TAIR,VDA,UHM,RA,RH,PCP,PA(L),PN(L),AW(L),VDS(L),S(L),
1 DWV(L),WAP(L),TA1(L),RNH3P,RNH3,JA(L),JB(L),JC(L)
1 /BLK9/MW,LHV,PAE,B1,SAND,SILT,CLAY,KSAT(L),B2,AT,BT,HT,
1 XT,CT,PDRAIN,KVP(L),KVT(L),KW(L),KH(L),EVAP,RAIN,
1 PRECIP,JW(L),JWC(L),ERR(L),FH,FU,FW,FO,GH,GU,GW,GO
C /BLK10/M,N,JJ,OCARB,DT,TDEPTH

DO 10 I=1,N
IF (JW(I) .GT. 0.0 .AND. JW(I+1) .GT. 0.0 .AND. JW(I+2) .GT. 0.0)
1 THEN
JWC(I)=JW(I)*CONC(I)-JW(I+1)*CONC(I+1)
JA(I)=FN*JW(I)
JB(I)=FN*JW(I+1)
JC(I)=0.0
ELSE IF (JW(I) .GT. 0.0 .AND. JW(I+1) .GT. 0.0 .AND. JW(I+2) .LT.
1 0.0) THEN

```

```

JWC(I)=JW(I)*CONC(I)-JW(I+1)*CONC(I+1)-JW(I+2)*CONC(I+2)
JA(I)=-FN*JW(I)
JB(I)=FN*JW(I+1)
JC(I)=FN*JW(I+2)
ELSE IF (JW(I) .GT. 0.0 .AND. JW(I+1) .LT. 0.0 .AND. JW(I+2) .GT.
1 0.0) THEN
JWC(I)=JW(I)*CONC(I)+JW(I+1)*CONC(I+1)
JA(I)=-FN*JW(I)
JB(I)=FN*JW(I+1)
JC(I)=0.0
ELSE IF (JW(I) .GT. 0.0 .AND. JW(I+1) .LT. 0.0 .AND. JW(I+2) .LT.
1 0.0) THEN
JWC(I)=JW(I)*CONC(I)+JW(I+1)*CONC(I+1)-JW(I+2)*CONC(I+2)
JA(I)=-FN*JW(I)
JB(I)=FN*JW(I+1)
JC(I)=FN*JW(I+2)
ELSE IF (JW(I) .GT. 0.0 .AND. JW(I+1) .EQ. 0.0 .AND. JW(I+2) .EQ.
1 0.0) THEN
JWC(I)=JW(I)*CONC(I)
JA(I)=-FN*JW(I)
JB(I)=0.0
JC(I)=0.0
ELSE IF (JW(I) .GT. 0.0 .AND. JW(I+1) .EQ. 0.0 .AND. JW(I+2) .LT.
1 0.0) THEN
JWC(I)=JW(I)*CONC(I)-JW(I+2)*CONC(I+2)
JA(I)=-FN*JW(I)
JB(I)=0.0
JC(I)=FN*JW(I+2)
ELSE IF (JW(I) .GT. 0.0 .AND. JW(I+1) .EQ. 0.0 .AND. JW(I+2) .GT.
1 0.0) THEN
JWC(I)=JW(I)*CONC(I)
JA(I)=-FN*JW(I)
JB(I)=0.0
JC(I)=0.0
ELSE IF (JW(I) .GT. 0.0 .AND. JW(I+1) .LT. 0.0 .AND. JW(I+2) .EQ.
1 0.0) THEN
JWC(I)=JW(I)*CONC(I)+JW(I+1)*CONC(I+1)
JA(I)=-FN*JW(I)
JB(I)=FN*JW(I+1)
JC(I)=0.0
ELSE IF (JW(I) .GT. 0.0 .AND. JW(I+1) .GT. 0.0 .AND. JW(I+2) .EQ.
1 0.0) THEN
JWC(I)=JW(I)*CONC(I)-JW(I+1)*CONC(I+1)
JA(I)=-FN*JW(I)
JB(I)=FN*JW(I+1)
JC(I)=0.0
ELSE IF (JW(I) .LT. 0.0 .AND. JW(I+1) .LT. 0.0 .AND. JW(I+2) .LT.
1 0.0) THEN
JWC(I)=JW(I+1)*CONC(I+1)-JW(I+2)*CONC(I+2)
JA(I)=0.0
JB(I)=FN*JW(I+1)
JC(I)=FN*JW(I+2)
ELSE IF (JW(I) .LT. 0.0 .AND. JW(I+1) .LT. 0.0 .AND. JW(I+2) .GT.
1 0.0) THEN
JWC(I)=JW(I+1)*CONC(I+1)
JA(I)=0.0
JB(I)=FN*JW(I+1)
JC(I)=0.0

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ELSE IF (JW(I) .LT. 0.0 .AND. JW(I+1) .LT. 0.0 .AND. JW(I+2) .EQ.
1 0.0) THEN
    JWC(I)=JW(I+1)*CONC(I+1)
    JA(I)=0.0
    JB(I)=-FN*JW(I+1)
    JC(I)=0.0
ELSE IF (JW(I) .LT. 0.0 .AND. JW(I+1) .GT. 0.0 .AND. JW(I+2) .LT.
1 0.0) THEN
    JWC(I)=-JW(I+1)*CONC(I+1)-JW(I+2)*CONC(I+2)
    JA(I)=0.0
    JB(I)=FN*JW(I+1)
    JC(I)=FN*JW(I+2)
ELSE IF (JW(I) .LT. 0.0 .AND. JW(I+1) .GT. 0.0 .AND. JW(I+2) .GT.
1 0.0) THEN
    JWC(I)=-JW(I+1)*CONC(I+1)
    JA(I)=0.0
    JB(I)=FN*JW(I+1)
    JC(I)=0.0
ELSE IF (JW(I) .LT. 0.0 .AND. JW(I+1) .EQ. 0.0 .AND. JW(I+2) .EQ.
1 0.0) THEN
    JWC(I)=0.0
    JA(I)=0.0
    JB(I)=0.0
    JC(I)=0.0
ELSE IF (JW(I) .LT. 0.0 .AND. JW(I+1) .EQ. 0.0 .AND. JW(I+2) .GT.
1 0.0) THEN
    JWC(I)=0.0
    JA(I)=0.0
    JB(I)=0.0
    JC(I)=0.0
ELSE IF (JW(I) .LT. 0.0 .AND. JW(I+1) .EQ. 0.0 .AND. JW(I+2) .LT.
1 0.0) THEN
    JWC(I)=-JW(I+2)*CONC(I+2)
    JA(I)=0.0
    JB(I)=0.0
    JC(I)=FN*JW(I+2)
ELSE IF (JW(I) .LT. 0.0 .AND. JW(I+1) .GT. 0.0 .AND. JW(I+2) .EQ.
1 0.0) THEN
    JWC(I)=-JW(I+1)*CONC(I+1)
    JA(I)=0.0
    JB(I)=FN*JW(I+1)
    JC(I)=0.0
ELSE IF (JW(I) .EQ. 0.0 .AND. JW(I+1) .EQ. 0.0 .AND. JW(I+2) .EQ.
1 0.0) THEN
    JWC(I)=0.0
    JA(I)=0.0
    JB(I)=0.0
    JC(I)=0.0
ELSE IF (JW(I) .EQ. 0.0 .AND. JW(I+1) .EQ. 0.0 .AND. JW(I+2) .GT.
1 0.0) THEN
    JWC(I)=0.0
    JA(I)=0.0
    JB(I)=0.0
    JC(I)=0.0
ELSE IF (JW(I) .EQ. 0.0 .AND. JW(I+1) .EQ. 0.0 .AND. JW(I+2) .LT.
1 0.0) THEN
    JWC(I)=-JW(I+2)*CONC(I+2)
    JA(I)=0.0
    JB(I)=0.0

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      JC(I)=FN*JW(I+2)
      ELSE IF (JW(I) .EQ. 0.0 .AND. JW(I+1) .GT. 0.0 .AND. JW(I+2) .EQ.
1 0.0) THEN
      JWC(I)=JW(I+1)*CONC(I+1)
      JA(I)=0.0
      JB(I)=FN*JW(I+1)
      JC(I)=0.0
      ELSE IF (JW(I) .EQ. 0.0 .AND. JW(I+1) .LT. 0.0 .AND. JW(I+2) .EQ.
1 0.0) THEN
      JWC(I)=JW(I+1)*CONC(I+1)
      JA(I)=0.0
      JB(I)=-FN*JW(I+1)
      JC(I)=0.0
      ELSE IF (JW(I) .EQ. 0.0 .AND. JW(I+1) .LT. 0.0 .AND. JW(I+2) .GT.
1 0.0) THEN
      JWC(I)=JW(I+1)*CONC(I+1)
      JA(I)=0.0
      JB(I)=-FN*JW(I+1)
      JC(I)=0.0
      ELSE IF (JW(I) .EQ. 0.0 .AND. JW(I+1) .LT. 0.0 .AND. JW(I+2) .LT.
1 0.0) THEN
      JWC(I)=JW(I+1)*CONC(I+1)-JW(I+2)*CONC(I+2)
      JA(I)=0.0
      JB(I)=-FN*JW(I+1)
      JC(I)=FN*JW(I+2)
      ELSE IF (JW(I) .EQ. 0.0 .AND. JW(I+1) .GT. 0.0 .AND. JW(I+2) .GT.
1 0.0) THEN
      JWC(I)=JW(I+1)*CONC(I+1)
      JA(I)=0.0
      JB(I)=FN*JW(I+1)
      JC(I)=0.0
      ELSE IF (JW(I) .EQ. 0.0 .AND. JW(I+1) .GT. 0.0 .AND. JW(I+2) .LT.
1 0.0) THEN
      JWC(I)=JW(I+1)*CONC(I+1)-JW(I+2)*CONC(I+2)
      JA(I)=0.0
      JB(I)=FN*JW(I+1)
      JC(I)=FN*JW(I+2)
      END IF
10 CONTINUE
      RETURN
      END

C
SUBROUTINE OUTPUT
C
*****
IMPLICIT REAL*8 (A-Z)
INTEGER*2 I,L,M,N,JJ,DT,DAY,HOUR,MIN
PARAMETER (L=50)
COMMON/BLK0/U(L),ANH4AQ(L),AUAQ(L),PERUH,LOSS,HYD,SHYD
1 /BLK5/NH4AQ(L),NH3AQ(L),HCO3(L),CO2AQ(L),H(L),MU(L),CA(L)
1 /BLK8/T(L),TA(L),TN(L),W(L),WA(L),BD(L),TSURF,HOUR,DAY,MIN
1 /BLK10/M,N,JJ,OCARB,DT,TDEPTH
1 /BLK11/NH4AD(L),NH4CO3(L),N4HCO3(L),NH3G(L),NH3LOS,CO2LOS
1 /BLK13/CO3(L),CO2G(L),CALC(L),NYIELD,CYIELD,NRECOV,CRECOV,HGEN
1 /BLK14/ADSH(L),HINIT,CAINIT,DNH4AQ(L),DHCO3(L),DNH3AQ(L),
1 DCO2AQ(L),DCO2G(L),DNH3G(L),CAACT,HACT,IADSH(L),CAAD(L)
C
      WRITE(5,175)
175 FORMAT('/// DAY',3X,'HOUR',3X,'MIN')

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      WRITE(5,185)DAY,HOUR,MIN
185  FORMAT(1X,I3,3X,I3,3X,I3)
      WRITE(5,195)
195  FORMAT(/' NH4AQ   NH3G   HCO3   CO2G   NH4AD   UREA
      1CA   WA   TA   PH')
      DO 2800 I = 1,M
      WRITE(5,2900)NH4AQ(I),NH3G(I+1),HCO3(I),CO2G(I+1),NH4AD(I),
      1 AUAQ(I+1),CA(I),WA(I),TA(I+1)-273.15,-LOG10(H(I))
2800  CONTINUE
      WRITE(5,2850)LOSS*100.0,PERUH
      WRITE(5,2950)NRECOV,CRECOV,HACT,CAACT
2850  FORMAT(/' % UREA-N LOSS =' ,E10.4,' , % UREA HYDROLYZED =' ,
      1 F7.2)
2900  FORMAT(E8.3,4E9.3,E10.4,E8.2,1X,F5.4,F6.1,1X,F5.2)
2950  FORMAT(' % N ACCOUNT=' ,F6.1,' ,% C ACCOUNT=' ,F6.1,
      1 ' ,% H ACCOUNT=' ,F6.1,' ,% CA ACCOUNT=' ,F6.1)
      RETURN
      END

```

DOCUMENTATION FOR PC MODEL

Constants

The following constants are defined by the PARAMETER statement in the model:

DW	density of water, kg/m^3
GR	acceleration due to gravity, m/s^2
KVON	von Karman constant, dimensionless
L	maximum value of a subscript, dimensionless
MA	molecular mass of air, kg/mol
R	gas constant, J/(mol)(K)
SBCST	Stefan-Boltzmann constant, $\text{W/(m}^2\text{)(K}^4\text{)}$

Parameters

The values for the following parameters are given in the input data file, PARAM.DAT:

APRATE	application rate of urea, kg urea-N/ha
ATOLER	tolerance for convergence of ammoniacal species mass balance, dimensionless
BTOLER	tolerance for convergence of carbonate species mass balance, dimensionless
CTOLER	tolerance for convergence of Ca^{2+} mass balance, dimensionless
DT	time step for new set of conditions, s
FOO2	correction factor for solubility of $\text{CO}_2(\text{g})$, dimensionless
FH	forward weighting factor for energy (temperature) balance, dimensionless

FN	forward weighting factor for mass balances of N, C, Ca^{2+} and H^+ , dimensionless
FNH3	correction factor for solubility of $\text{NH}_3(\text{g})$, dimensionless
FO	forward weighting factor in iteration for energy (temperature) balance, dimensionless
FRAC	gas-film mass transfer resistance for $\text{CO}_2(\text{g})$, expressed as a fraction of the overall resistance, dimensionless
FSBC	a multiplying factor for varying H^+ -buffering capacity of soil, dimensionless
FU	forward weighting factor for urea mass balance, dimensionless
FW	forward weighting factor for soil water flux (water potential) balance, dimensionless
HCO2	sink term in H^+ balance due $\text{CO}_2(\text{g})$ loss from soil surface, $\text{kmol}/(\text{m}^2 \text{ soil})(\text{s})$
HNH3	source term in N-balance due $\text{NH}_3(\text{g})$ loss from soil surface, $\text{kmol}/(\text{m}^2 \text{ soil})(\text{s})$
HTOLER	tolerance for convergence of H^+ mass balance, dimensionless
IPH	initial soil pH, dimensionless
ITER	maximum number of iterations allowed in mass balances for N, C, Ca^{2+} and H^+ , dimensionless
M	number of nodes or number of soil depth increments from surface to total modeled soil depth, dimensionless
NK1	Freundlich equation coefficient, dimensionless
NK2	exponent in Freundlich equation, dimensionless
OCARB	organic carbon content of soil, %
SCO2	initial concentration of $\text{CO}_2(\text{g})$ in the surface layer of soil, $\text{kmol}/\text{m}^3 \text{ soil air}$
SRESP	soil respiration rate for the surface layer of soil, $\text{kmol}/(\text{m}^3 \text{ soil})(\text{s})$
TCA	total Ca^{2+} in soil, mg/kg
TDEPTH	total modeled soil depth, m

Soil Characteristics

The values for the following are given in the soil characteristics file, HAYNIE.DAT:

A1	coefficient of first term in soil buffering capacity equation, dimensionless
A2	coefficient of second term in soil buffering capacity equation, dimensionless
A3	coefficient of third term in soil buffering capacity equation, dimensionless
A4	constant of integration for soil buffering capacity equation, kmol/kg soil
AT	thermal conductivity constant, $W/(m)(K)$
B1	characteristic soil moisture curve constant, dimensionless
BT	thermal conductivity constant, $W/(m^2)(K)$
CLAY	fraction clay content of soil, dimensionless
HT	thermal conductivity constant, $W/(m)(K)$
PAE	air entry potential, J/kg
PDRAIN	precipitation added at this potential, J/kg (not used in the PC Model)
SAND	fraction sand content of soil, dimensionless
SILT	fraction silt content of soil, dimensionless
XT	thermal conductivity constant, dimensionless

Variables

The following variables are defined for the model, in general:

AE	Arrhenius constant, J/mol
ALBEDO	soil surface reflectivity, dimensionless
B2	hydraulic conductivity constant, dimensionless

BETA	hydrogen-ion buffering capacity of soil, $\text{kmol OH}^-/(\text{kg soil})(\text{pH})$
C1	product of Ca^{2+} and CO_3^{2-} concentrations minus $\text{CaCO}_3(\text{s})$ solubility product constant, $(\text{kmol/m}^3 \text{ soil sol})^2$
CAACT	percent initial Ca^{2+} accounted, %
CAADNU	Ca^{2+} in the adsorbed phase at any given time, $\text{kmol/m}^3 \text{ soil}$
CAINIT	total initial Ca^{2+} in solution, in the adsorbed phase and as $\text{CaCO}_3(\text{s})$, $\text{kmol/m}^3 \text{ soil}$
CANEW	Ca^{2+} in solution at any given time, $\text{kmol/m}^3 \text{ soil}$
CBAL	sum of carbon in unhydrolyzed urea, total $\text{CO}_2(\text{g})$ lost and total carbon change in soil, $\text{kmol/m}^2 \text{ soil}$
CHECK	product of Ca^{2+} and CO_3^{2-} concentrations, $(\text{kmol/m}^3 \text{ soil sol})^2$
CHYD	carbon in cumulative urea hydrolyzed, $\text{kmol/m}^2 \text{ soil}$
CLOS	cumulative $\text{CO}_2(\text{g})$ loss, $\text{kmol/m}^2 \text{ soil}$
CLCNEW	Ca^{2+} as $\text{CaCO}_3(\text{s})$ at any given time, $\text{kmol/m}^3 \text{ soil}$
CLDCOV	fraction of cloud cover, dimensionless
CO2LOS	$\text{CO}_2(\text{g})$ loss from soil surface, $\text{kmol}/(\text{m}^2 \text{ soil})(\text{s})$
CO2RES	$\text{CO}_2(\text{g})$ respired in time interval DT, $\text{kmol/m}^2 \text{ soil}$
COEFF	a multiplying factor (less than unity) to decrease change in temperature or water potential for an iteration, dimensionless
COUNT	iteration counter, dimensionless
CRECOV	carbon accounted on a cumulative basis, %
CT	thermal conductivity constant, dimensionless
CYIELD	carbon accounted on a time-step basis, %
DA	density of air, kg/m^3
DAY	Julian day
DCT	cumulative carbon change in soil, $\text{kmol/m}^2 \text{ soil}$
DELTA	$\text{CaCO}_3(\text{s})$ precipitated or dissolved in time interval DT, $\text{kmol/m}^2 \text{ soil}$

DH	change in H^+ in soil solution in time interval DT, kmol/m^3 soil
DNT	cumulative change in N in soil, kmol/m^2 soil
DTC	change in carbon in soil in time interval DT, kmol/m^2 soil
DTN	change in N in soil in time interval DT, kmol/m^2 soil
DU	diffusivity of urea in water, m^2 soil sol/s
DVAL	correction increment to new value in iteration, variable dimensions
EA	emissivity of atmosphere, dimensionless
ERRH	total absolute error in energy (temperature) balance, W/m^3
ERRW	total absolute error in soil water flux (water potential) balance, m/s
ES	emissivity of soil surface, dimensionless
ETA	enhancement factor --- thermal conductivity, dimensionless
ETA1	enhancement factor --- thermal conductivity, dimensionless
ETA2	enhancement factor --- thermal conductivity, dimensionless
EVAP	evaporation rate, m/s
FC	stability term, dimensionless
FCLOSE	logical variable to check end of meteorological data file, dimensionless
FLAG	convergence check counter, dimensionless
G1	sum of the concentrations of Ca^{2+} and CO_3^{2-} , kmol/m^3 soil sol
GH	backward weighting factor for energy (temperature) balance, dimensionless
GN	backward weighting factor for mass balances of N, C, Ca^{2+} and H^+ , dimensionless
GO	backward weighting factor in iteration for energy (temperature) balance, dimensionless
GU	backward weighting factor for urea mass balance, dimensionless

GW	backward weighting factor for soil water flux (water potential) balance, dimensionless
HACT	percent of initial H^+ accounted, %
HADSNU	H^+ in the adsorbed phase at any given time, kmol/m^3 soil
HGEN	cumulative H^+ generated, kmol/m^3 soil
HINIT	total initial H^+ in solution and in the adsorbed phase, kmol/m^3 soil
HM	height of atmospheric measurements, m
HNEW	H^+ in solution at any given time, kmol/m^3 soil
HOURL	hour of day
HYD	cumulative amount of urea hydrolyzed at any given time, kmol/m^2 soil
I	subscript of array, dimensionless
J	subscript of array, dimensionless
JJ	subscript of array, dimensionless
KC	$\text{CaCO}_3(\text{s})$ solubility product constant, $(\text{kmol/m}^3 \text{ soil sol})^2$
KHC	thermal conductivity at node, W/(m)(K)
KHC1	thermal conductivity at node, W/(m)(K)
KHC2	thermal conductivity at node, W/(m)(K)
KHT	thermal conductivity of previous node, W/(m)(K)
KK	subscript of array, dimensionless
KM	Michaelis-Menten constant for rate of urea hydrolysis, kmol/m^3 soil sol
KP	isothermal vapor conductivity, $(\text{kg})(\text{s})/\text{m}^3$
KT	thermal vapor conductivity, kg/(m)(s)(K)
LHV	latent heat of vaporization of water, J/kg
LN	natural logarithm of the ratio of height of atmospheric measurements to roughness length, dimensionless

LOSS	ammonia-N loss expressed as a percent of urea-N applied, %
M310	urea hydrolysis rate at 310 K, $\text{kmol}/(\text{kg soil})(\text{s})$
MAXVAL	upper limit of applicable value for convergence, variable dimensions
MFLAG	counter to permit initialization of concentrations or to bypass initialization, dimensionless
MIN	minutes past the hour
MINVAL	lower limit of applicable value for convergence, variable dimensions
MW	molecular mass of water, kg/mol
MWU	molecular mass of urea, kg/kmol
N	subscript of array, dimensionless
NBAL	sum of N in unhydrolyzed urea, total $\text{NH}_3(\text{g})$ lost and total N change in soil, $\text{kmol}/\text{m}^2 \text{ soil}$
NHYD	N in cumulative urea hydrolyzed, $\text{kmol}/\text{m}^2 \text{ soil}$
NFLAG	counter that permits change in number of nodes in subroutine SOLVE
NH3LOS	$\text{NH}_3(\text{g})$ loss from soil surface, $\text{kmol}/(\text{m}^2)(\text{s})$
NLOS	cumulative $\text{NH}_3(\text{g})$ loss, $\text{kmol}/\text{m}^2 \text{ soil}$
NSUM	total error in mass balances for N, C, Ca^{2+} , H^+ and urea, $\text{kmol}/(\text{m}^2)(\text{s})$
NYIELD	N accounted on a time-step basis, %
PCP	volumetric heat capacity of air, J/m^3
PEFF	factor to account for effect of soil moisture on urea hydrolysis rate, dimensionless
PHEFF	factor to account for effect of pH on urea hydrolysis rate, dimensionless
PERUH	cumulative urea hydrolyzed, %
PRECIP	depth of precipitation or irrigation, mm
RA	resistance to mass transfer for water vapor, s/m

RAIN	depth of precipitation, mm
RAOLD	value of RA in previous iteration, s/m
RESP	cumulative $\text{CO}_2(\text{g})$ respired, kmol/m^2 soil
RH	resistance to heat transfer, s/m
RHOLD	value of RH in previous iteration, s/m
RNH3	resistance to mass transfer for $\text{NH}_3(\text{g})$, s/m
RNH3P	value of RNH3 in previous time step, s/m
RSW	reflected short wave radiation, W/m^2
SFLUX	soil water flux in surface layer of soil, m^3 soil sol/(m^2 soil)(s)
SHF	heat flux, W/m^2
SHYD	urea hydrolyzed at surface in time interval DT expressed as a percent of total urea hydrolyzed in time interval DT, %
START	counter to permit initialization of urea concentration at soil surface, dimensionless
SUM1	total error in N-balance, summed for all nodes for time interval DT, $\text{kmol}/(\text{m}^2)(\text{s})$
SUM2	total error in C-balance, summed for all nodes for time interval DT, $\text{kmol}/(\text{m}^2)(\text{s})$
SUM3	total error in Ca^{2+} -balance, summed for all nodes for time interval DT, $\text{kmol}/(\text{m}^2)(\text{s})$
SUM4	total error in H^+ -balance, summed for all nodes for time interval DT, $\text{kmol}/(\text{m}^2)(\text{s})$
SW	incident short wave radiation, W/m^2
T6CM	measured soil temperature at 6-cm depth, K
T15CM	measured soil temperature at 15-cm depth, K
T30CM	measured soil temperature at 30-cm depth, K
TAIR	measured air temperature at height HM above surface, K
TDH	cumulative change in H^+ in soil solution, summed for all nodes, kmol/m^3 soil

TDHADS	cumulative change in H^+ adsorbed, summed for all nodes, kmol/m^3 soil
TERR	total error in energy (temperature) balance, summed for all nodes, W/m^3
THETA	average air temperature, K
TLOSS	cumulative ammonia-N loss, kmol/m^2 soil
TOTALU	total urea applied, kmol/m^2 soil
TP	total atmospheric pressure, Pa
TSURF	measured soil surface temperature, K
UERR	total absolute relative error in urea mass balance, dimensionless
UHM	wind speed at height HM above surface, m/s
UHYD	urea hydrolyzed in time interval DT, kmol/m^2 soil
UNHYD	unhydrolyzed urea, kmol/m^2 soil
USAT	solubility of urea, kmol/m^3 soil sol
USTAR	friction velocity, m/s
V	urea hydrolysis rate, $\text{kmol}/(\text{kg soil})(\text{s})$
VDA	vapor density of air, kg/m^3
VM	empirical constant for urea hydrolysis rate, $\text{kmol}/(\text{kg soil})(\text{s})$
VMAX	maximum urea hydrolysis rate at a given temperature, $\text{kmol}/(\text{kg soil})(\text{s})$
VP	vapor pressure of water, Pa
WERR	total error in soil water flux (water potential) balance, m/s
XC	stability term, dimensionless
Y	stability term, dimensionless
ZETA	ratio of HM to Monin-Obukhov length, dimensionless
ZO	roughness length, m

Arrays

The following arrays are defined for the model, in general:

A	partial derivative of F_i with respect to the unknown value for node $i-1$, variable dimensions
ACA	weighted-average concentration of Ca^{2+} , kmol/m^3 soil sol
ACALC	weighted-average concentration of $\text{CaCO}_3(\text{s})$ kmol/m^3 soil sol
ACO2AQ	weighted-average concentration of $\text{CO}_2(\text{aq})$, kmol/m^3 soil sol
ACO3	weighted-average concentration of CO_3^{2-} kmol/m^3 soil sol
ADS	NH_4^+ adsorbed/desorbed in time interval DT , kmol/kg soil
ADSH	H^+ adsorbed/desorbed in time interval DT , kmol/kg soil
AH	weighted-average concentration of H^+ kmol/m^3 soil sol
AHCO3	weighted-average concentration of HCO_3^- kmol/m^3 soil sol
ANH3AQ	weighted-average concentration of $\text{NH}_3(\text{aq})$ kmol/m^3 soil sol
ANH4AQ	weighted-average concentration of NH_4^+ kmol/m^3 soil sol
AOH	weighted-average concentration of OH^- kmol/m^3 soil sol
AUAQ	weighted-average concentration of urea kmol/m^3 soil sol
AW	activity of water, dimensionless
B	partial derivative of F_i with respect to the unknown value for node i , variable dimensions
BD	bulk density of soil, Mg/m^3
C	partial derivative of F_i with respect to the unknown value for node $i+1$, variable dimensions
CA	concentration of Ca^{2+} in solution at the beginning of a time-step, kmol/m^3 soil sol
CAAD	concentration of Ca^{2+} in the adsorbed phase at the beginning of a time-step, kmol/kg soil
CALC	concentration of $\text{CaCO}_3(\text{s})$ at the beginning of a time-step, kmol/m^3 soil sol

CAP	capacity term associated with a node, variable dimensions
CO2AQ	concentration of $\text{CO}_2(\text{aq})$ at the beginning of a time-step, kmol/m^3 soil sol
CO2G	weighted average concentration of $\text{CO}_2(\text{g})$, kmol/m^3 soil air
CONC	weighted average concentration of applicable chemical species, kmol/m^3 soil sol
D	diffusivity of applicable chemical species in soil, $\text{m}^2 \text{ soil sol}/(\text{m}^2 \text{ soil})(\text{s})$
D1	diffusivity of H^+ in water, $\text{m}^2 \text{ soil sol/s}$
D2	diffusivity of OH^- in water, $\text{m}^2 \text{ soil sol/s}$
D4	diffusivity of $\text{NH}_3(\text{g})$ in air, $\text{m}^2 \text{ soil air/s}$
D5	diffusivity of $\text{NH}_3(\text{aq})$ in water, $\text{m}^2 \text{ soil sol/s}$
D7	diffusivity of NH_4^+ in water, $\text{m}^2 \text{ soil sol/s}$
D8	diffusivity of NH_4CO_3^- in water, $\text{m}^2 \text{ soil sol/s}$
D9	diffusivity of $\text{NH}_4\text{HCO}_3^0$ in water, $\text{m}^2 \text{ soil sol/s}$
D10	diffusivity of $\text{CO}_2(\text{g})$ in air, $\text{m}^2 \text{ soil air/s}$
D11	diffusivity of $\text{CO}_2(\text{aq})$ in water, $\text{m}^2 \text{ soil sol/s}$
D12	diffusivity of CO_3^{2-} in water, $\text{m}^2 \text{ soil sol/s}$
D13	diffusivity of HCO_3^- in water, $\text{m}^2 \text{ soil sol/s}$
D14	diffusivity of Ca^{2+} in water, $\text{m}^2 \text{ soil sol/s}$
DCALC	change in $\text{CaCO}_3(\text{s})$ in time interval DT, kmol/m^3 soil
DCO2AQ	change in $\text{CO}_2(\text{aq})$ in time interval DT, kmol/m^3 soil
DCO2G	change in $\text{CO}_2(\text{g})$ in time interval DT, kmol/m^3 soil
DCO3	change in CO_3^{2-} in time interval DT, kmol/m^3 soil
DHCO3	change in HCO_3^- in time interval DT, kmol/m^3 soil
DNH3AQ	change in $\text{NH}_3(\text{aq})$ in time interval DT, kmol/m^3 soil
DNH4AD	change in $\text{NH}_4^+(\text{ad})$ in time interval DT, kmol/m^3 soil

DNH4AQ	change in NH_4^+ in time interval DT, kmol/m^3 soil
DNH4C3	change in NH_4CO_3^- in time interval DT, kmol/m^3 soil
DN4HC3	change in $\text{NH}_4\text{HCO}_3^0$ in time interval DT, kmol/m^3 soil
DWV	diffusivity of water vapor in air, m^2/s
ERR	error in urea mass balance for a node, $\text{kmol}/(\text{m}^2 \text{ soil})(\text{s})$
F	value of mass balance, energy balance or soil water flux balance function in Newton-Raphson Method, variable dimensions
FA	air-filled porosity of soil, m^3 soil air/ m^3 soil
H	concentration of H^+ at beginning of time-step, kmol/m^3 soil sol
HADS	source/sink term in H^+ balance to account for NH_4^+ adsorption/desorption, $\text{kmol}/(\text{m}^2 \text{ soil})(\text{s})$
HCALC	source/sink term in H^+ balance to account for $\text{CaCO}_3(\text{s})$ precipitation/dissolution, $\text{kmol}/(\text{m}^2 \text{ soil})(\text{s})$
HCO3	concentration of HCO_3^- at the beginning of a time step, kmol/m^3 soil sol
HRESP	source term in H^+ balance to account for $\text{CO}_2(\text{g})$ production from soil respiration, $\text{kmol}/(\text{m}^2 \text{ soil})(\text{s})$
HSINK	net sink term in H^+ balance, $\text{kmol}/(\text{m}^2 \text{ soil})(\text{s})$
IADSH	amount of H^+ in the adsorbed phase at the beginning of a time step, kmol/m^3 soil
ICALC	amount of $\text{CaCO}_3(\text{s})$ at the beginning of a time step, kmol/m^3 soil
ICO2AQ	amount of $\text{CO}_2(\text{aq})$ at the beginning of a time step, kmol/m^3 soil
ICO2G	amount of $\text{CO}_2(\text{g})$ in soil air at the beginning of a time step, kmol/m^3 soil
ICO3	amount of CO_3^{2-} at the beginning of a time step, kmol/m^3 soil
IH	amount of H^+ in solution at the beginning of a time step, kmol/m^3 soil
IHCO3	amount of HCO_3^- at the beginning of a time step, kmol/m^3 soil
INH3AQ	amount of $\text{NH}_3(\text{aq})$ at the beginning of a time step, kmol/m^3 soil

- INH3G amount of $\text{NH}_3(\text{g})$ in soil air at the beginning of a time step, kmol/m^3 soil
- INH4AD amount of NH_4^+ in the adsorbed phase at the beginning of a time step, kmol/m^3 soil
- INH4AQ amount of NH_4^+ in solution at the beginning of a time step, kmol/m^3 soil
- INH4C3 amount of NH_4CO_3^- at the beginning of a time step, kmol/m^3 soil
- IN4HC3 amount of $\text{NH}_4\text{HCO}_3^0$ at the beginning of a time step, kmol/m^3 soil
- JA partial derivative of the convective flux of applicable chemical species, for node i, with respect to the concentration of the species for node i-1, m^3 soil sol/ $(\text{m}^2$ soil)(s)
- JB partial derivative of the convective flux of applicable chemical species, for node i, with respect to the concentration of the species for node i, m^3 soil sol/ $(\text{m}^2$ soil)(s)
- JC partial derivative of the convective flux of applicable chemical species, for node i, with respect to the concentration of the species for node i+1, m^3 soil sol/ $(\text{m}^2$ soil)(s)
- JCO2AQ convective flux of $\text{CO}_2(\text{aq})$, $\text{kmol}/(\text{m}^2$ soil)(s)
- JH convective flux of H^+ , $\text{kmol}/(\text{m}^2$ soil)(s)
- JHCO3 convective flux of HCO_3^- , $\text{kmol}/(\text{m}^2$ soil)(s)
- JNH4AQ convective flux of NH_4^+ , $\text{kmol}/(\text{m}^2$ soil)(s)
- JW soil water flux, m^3 soil sol/ $(\text{m}^2$ soil)(s)
- JWC convective flux of applicable chemical species, $\text{kmol}/(\text{m}^2$ soil)(s)
- KO ion product constant for water, $(\text{kmol}/\text{m}^3 \text{ soil sol})^2$
- K1 Henry's Law constant for equilibrium between $\text{NH}_3(\text{aq})$ and $\text{NH}_3(\text{g})$, $(\text{kmol}/\text{m}^3 \text{ soil sol})(\text{kmol}/\text{m}^3 \text{ soil air})^{-1}$
- K2 equilibrium constant for equilibrium between NH_4^+ , $\text{NH}_3(\text{aq})$ and H^+ , $\text{kmol}/\text{m}^3 \text{ soil sol}$
- K4 equilibrium constant for equilibrium between NH_4^+ , HCO_3^- and $\text{NH}_4\text{HCO}_3^0$, $\text{kmol}/\text{m}^3 \text{ soil sol}$

K5	equilibrium constant for equilibrium between NH_4^+ , CO_3^{2-} and NH_4CO_3^- , kmol/m^3 soil sol
K7	Henry's Law constant for equilibrium between $\text{CO}_2(\text{aq})$ and $\text{CO}_2(\text{g})$, $(\text{kmol/m}^3 \text{ soil sol})(\text{kmol/m}^3 \text{ soil air})^{-1}$
K8	equilibrium constant for equilibrium between HCO_3^- , $\text{CO}_2(\text{aq})$ and H^+ , kmol/m^3 soil sol
K9	equilibrium constant for equilibrium between HCO_3^- , CO_3^{2-} and H^+ , kmol/m^3 soil sol
K11	solubility product constant for $\text{CaCO}_3(\text{s})$, $(\text{kmol/m}^3 \text{ soil sol})^2$
KH	thermal conductance, $\text{W}/(\text{m}^2)(\text{K})$
KSAT	saturated hydraulic conductivity, s
KVP	isothermal vapor conductance, $(\text{kg})(\text{s})/(\text{m}^4)$
KVT	thermal vapor conductance, $\text{kg}/(\text{m}^2)(\text{s})/(\text{K})$
KW	hydraulic conductance, s/m
MASS	mass associated with a node, kg/m^2 soil
NADSH	concentration of H^+ in the adsorbed phase at the end of time step, kmol/kg soil
NCA	concentration of Ca^{2+} at the end of time step, kmol/m^3 soil sol
NCAAD	concentration of Ca^{2+} in the adsorbed phase at the end of time step, kmol/kg soil
NCALC	concentration of $\text{CaCO}_3(\text{s})$ at the end of time step, kmol/m^3 soil sol
NEWVAL	new value, as applicable, at the end of time step, variable dimensions
NH	concentration of H^+ at the end of time step, kmol/m^3 soil sol
NH3AQ	concentration of $\text{NH}_3(\text{aq})$ at the beginning of time step, kmol/m^3 soil sol
NH3G	weighted average concentration of $\text{NH}_3(\text{g})$ for time step, kmol/m^3 soil air
NHCO3	concentration of HCO_3^- at the end of time step, kmol/m^3 soil sol

NH4AD	concentration of NH_4^+ in the adsorbed phase at the end of time step, kmol/kg soil
NH4CO3	concentration of NH_4CO_3^- at the end of time step, $\text{kmol/m}^3 \text{ soil sol}$
N4HCO3	concentration of $\text{NH}_4\text{HCO}_3^0$ at the end of time step, $\text{kmol/m}^3 \text{ soil sol}$
NNH4AQ	concentration of NH_4^+ in solution at the end of time step, $\text{kmol/m}^3 \text{ soil sol}$
NUAQ	concentration of urea at the end of time step, $\text{kmol/m}^3 \text{ soil sol}$
P1	partial derivative of H^+ concentration in adsorbed phase with respect to H^+ concentration in solution, $(\text{kmol/kg soil})(\text{kmol/m}^3 \text{ soil sol})^{-1}$
P2	partial derivative of OH^- concentration with respect to H^+ concentration, dimensionless
P4	partial derivative of $\text{NH}_3(\text{g})$ concentration with respect to NH_4^+ concentration, $(\text{kmol/m}^3 \text{ soil air})(\text{kmol/m}^3 \text{ soil solution})^{-1}$
P5	partial derivative of $\text{NH}_3(\text{aq})$ concentration with respect to NH_4^+ concentration, dimensionless
P6	partial derivative of NH_4^+ concentration in adsorbed phase with respect to NH_4^+ concentration in solution, $(\text{kmol/kg soil})(\text{kmol/m}^3 \text{ soil sol})^{-1}$
P8	partial derivative of NH_4CO_3^- concentration with respect to NH_4^+ concentration, dimensionless
P9	partial derivative of $\text{NH}_4\text{HCO}_3^0$ concentration with respect to NH_4^+ concentration, dimensionless
P10	partial derivative of $\text{CO}_2(\text{g})$ concentration with respect to HCO_3^- concentration, $(\text{kmol/m}^3 \text{ soil air})(\text{kmol/m}^3 \text{ soil solution})^{-1}$
P11	partial derivative of $\text{CO}_2(\text{aq})$ concentration with respect to HCO_3^- concentration, dimensionless
P12	partial derivative of CO_3^{2-} concentration with respect to HCO_3^- concentration, dimensionless
P13	partial derivative of NH_4CO_3^- concentration with respect to HCO_3^- concentration, dimensionless
P14	partial derivative of $\text{NH}_4\text{HCO}_3^0$ concentration with respect to HCO_3^- concentration, dimensionless

P	water potential at the beginning of time step, J/kg
PA	weighted average water potential for time step, J/kg
PN	water potential at the end of time step, J/kg
POROS	total porosity of soil, dimensionless
RELW	water content relative to saturation, dimensionless
RESPIR	soil respiration rate, $\text{kmol}/(\text{m}^2 \text{ soil})(\text{s})$
S	slope of saturation vapor density temperature function, $\text{kg}/(\text{m}^3)(\text{K})$
T	soil temperature at beginning of time step, K
TA	weighted average soil temperature for time step, K
TAI	weighted average soil temperature in iteration for time step, K
TN	soil temperature at end of time step, K
U	source/sink term in mass, energy and soil water flux balances, variable dimensions
UAQ	concentration of urea at beginning of time step, $\text{kmol}/\text{m}^3 \text{ soil}$
UCA	rate of $\text{CaCO}_3(\text{s})$ precipitation or dissolution, $\text{kmol}/(\text{m}^2 \text{ soil})(\text{s})$
UCAAD	rate of Ca^{2+} adsorption or desorption, $\text{kmol}/(\text{m}^2 \text{ soil})(\text{s})$
USOLID	concentration of urea in solid phase, $\text{kmol}/\text{m}^2 \text{ soil}$
VDS	vapor density of air at saturation, kg/m^3
VOL	volume associated with a node, $\text{m}^3 \text{ soil}/\text{m}^2 \text{ soil}$
W	soil water content at beginning of time step, $\text{m}^3 \text{ soil sol}/\text{m}^3 \text{ soil}$
WA	weighted average soil water content for time step, $\text{m}^3 \text{ soil sol}/\text{m}^3 \text{ soil}$
WAP	weighted average soil water content for previous time step, $\text{m}^3 \text{ soil sol}/\text{m}^3 \text{ soil}$
Z	depth of a node from surface, m

APPENDIX C

Table 1. Model output file for standard run

MODELING PARAMETERS

M	ITER	DT	FH	FN	FU	FW	FO	TDEPTH	ATOLER	BTOLER	CTOLER	HTOLER
15	15	300	.60	.60	.60	.60	.85	.150	.5E-15	.5E-13	.5E-11	.5E-17

SENSITIVITY PARAMETERS

IPH	TCA	OCARB	APRATE	SRESP	NK1	NK2	FOO2	FNH3	FSBC	FRAC	SC02
6.4	1800.	1.04	120.	.28E-07	.19E-02	.66	10.0	10.0	1.00	.0050	.14E-03

Z	BD	W	T
.0000	1.155	.050	300.1
.0100	1.165	.065	300.7
.0200	1.175	.079	301.2
.0300	1.185	.092	301.6
.0400	1.195	.104	301.9
.0500	1.205	.115	302.1
.0600	1.215	.125	302.3
.0700	1.225	.134	302.1
.0800	1.235	.142	301.9
.0900	1.245	.149	301.6
.1000	1.255	.155	301.3
.1100	1.265	.160	301.0
.1200	1.275	.164	300.7
.1300	1.285	.167	300.4
.1400	1.295	.169	300.2

SOIL CHARACTERISTICS

B1	PAE	PDRAIN	SAND	SILT	CLAY	AT	BT	HT	XT	A1	A2	A3	A4
3.2	-1.4	-2.5	.65	.28	.07	.45	.90	.20	6.	.87E-05	.13E-03	.47E-03	.21E-02

DAY HOUR MIN
180 20 0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.100E-11	.986E-17	.130E-02	.142E-03	.228E-10	.0000E+00	.65E-03	.0576	27.3	6.40
.100E-11	.102E-16	.106E-02	.116E-03	.228E-10	.0000E+00	.53E-03	.0757	27.6	6.40
.100E-11	.107E-16	.863E-03	.952E-04	.228E-10	.0000E+00	.43E-03	.0928	28.0	6.40
.100E-11	.111E-16	.704E-03	.779E-04	.228E-10	.0000E+00	.35E-03	.1091	28.4	6.40
.100E-11	.115E-16	.574E-03	.638E-04	.228E-10	.0000E+00	.29E-03	.1243	28.7	6.40
.100E-11	.117E-16	.469E-03	.522E-04	.228E-10	.0000E+00	.23E-03	.1387	28.9	6.40
.100E-11	.119E-16	.384E-03	.428E-04	.228E-10	.0000E+00	.19E-03	.1520	29.0	6.40
.100E-11	.117E-16	.315E-03	.350E-04	.228E-10	.0000E+00	.16E-03	.1643	28.9	6.40
.100E-11	.115E-16	.258E-03	.287E-04	.228E-10	.0000E+00	.13E-03	.1755	28.7	6.40
.100E-11	.112E-16	.212E-03	.235E-04	.228E-10	.0000E+00	.11E-03	.1856	28.4	6.40
.100E-11	.108E-16	.174E-03	.192E-04	.228E-10	.0000E+00	.87E-04	.1946	28.1	6.40
.100E-11	.105E-16	.143E-03	.157E-04	.228E-10	.0000E+00	.71E-04	.2024	27.8	6.40
.100E-11	.102E-16	.117E-03	.129E-04	.228E-10	.0000E+00	.59E-04	.2090	27.5	6.40
.100E-11	.984E-17	.965E-04	.105E-04	.228E-10	.0000E+00	.48E-04	.2139	27.2	6.40
.100E-11	.953E-17	.793E-04	.864E-05	.228E-10	.0000E+00	.40E-04	.2189	27.0	6.40

% NH3-N LOSS = .0000E+00, % UREA HYDROLYZED = .00
% N ACCOUNT= .0, % C ACCOUNT= .0, % H ACCOUNT= .0, % CA ACCOUNT= .0

UHM	TSURF	TAIR	T5CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
.72	19.4	22.0	22.9	25.7	24.8	.0	.0	.01714	.00	.00	112854.	1000.

DAY HOUR MIN
181 0 0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.728E-05	.415E-10	.887E-03	.822E-04	.763E-06	.7866E+00	.88E-02	.0537	21.3	6.44
.687E-06	.377E-11	.883E-03	.913E-04	.162E-06	.1260E-02	.18E-02	.0770	21.9	6.40
.551E-10	.318E-15	.874E-03	.927E-04	.321E-09	.2352E-05	.45E-03	.0957	22.5	6.39
.104E-11	.642E-17	.861E-03	.920E-04	.234E-10	.5303E-08	.36E-03	.1139	23.2	6.39
.100E-11	.658E-17	.845E-03	.908E-04	.228E-10	.1366E-10	.30E-03	.1316	23.7	6.39
.100E-11	.694E-17	.826E-03	.890E-04	.228E-10	.3886E-13	.24E-03	.1475	24.2	6.39
.100E-11	.725E-17	.804E-03	.868E-04	.228E-10	.1184E-15	.19E-03	.1607	24.6	6.39
.100E-11	.753E-17	.779E-03	.844E-04	.228E-10	.3752E-18	.15E-03	.1713	24.9	6.39
.100E-11	.777E-17	.755E-03	.818E-04	.228E-10	.1206E-20	.12E-03	.1794	25.2	6.39
.100E-11	.796E-17	.730E-03	.792E-04	.228E-10	.3860E-23	.99E-04	.1855	25.4	6.39
.100E-11	.812E-17	.708E-03	.768E-04	.228E-10	.1211E-25	.80E-04	.1898	25.6	6.40
.100E-11	.823E-17	.689E-03	.747E-04	.228E-10	.3680E-28	.65E-04	.1926	25.7	6.40
.100E-11	.830E-17	.674E-03	.730E-04	.228E-10	.1071E-30	.54E-04	.1939	25.7	6.40
.100E-11	.832E-17	.663E-03	.718E-04	.228E-10	.2948E-33	.48E-04	.1938	25.8	6.40
.100E-11	.831E-17	.658E-03	.711E-04	.228E-10	.7596E-36	.40E-04	.1925	25.7	6.40

% NH3-N LOSS = .5134E-04, % UREA HYDROLYZED = 1.25
% N ACCOUNT= 100.0, % C ACCOUNT= 100.1, % H ACCOUNT= 100.0, % CA ACCOUNT= 100.0

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
.94	17.4	20.2	20.5	23.5	24.1	3.3	.6	.01598	.00	.00	86441.	1000.

DAY	HOUR	MIN
181	6	0

NH4AQ	NH3C	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.222E-04	.100E-09	.148E-02	.119E-03	.160E-05	.7346E+00	.18E-01	.0564	18.2	6.49
.383E-05	.148E-10	.148E-02	.147E-03	.504E-06	.1997E-02	.42E-02	.0801	18.7	6.40
.773E-09	.298E-14	.147E-02	.156E-03	.184E-08	.6288E-05	.50E-03	.1035	19.2	6.38
.145E-11	.596E-17	.146E-02	.156E-03	.292E-10	.2795E-07	.38E-03	.1258	19.8	6.38
.100E-11	.437E-17	.145E-02	.155E-03	.229E-10	.1561E-09	.29E-03	.1427	20.3	6.38
.100E-11	.461E-17	.143E-02	.153E-03	.228E-10	.9854E-12	.23E-03	.1549	20.8	6.38
.100E-11	.485E-17	.141E-02	.151E-03	.228E-10	.6594E-14	.18E-03	.1640	21.2	6.38
.100E-11	.510E-17	.139E-02	.149E-03	.228E-10	.4507E-16	.14E-03	.1707	21.6	6.38
.100E-11	.533E-17	.137E-02	.146E-03	.228E-10	.3075E-18	.11E-03	.1758	22.0	6.38
.100E-11	.555E-17	.135E-02	.144E-03	.228E-10	.2062E-20	.92E-04	.1794	22.3	6.39
.100E-11	.576E-17	.133E-02	.142E-03	.228E-10	.1343E-22	.75E-04	.1819	22.6	6.39
.100E-11	.596E-17	.131E-02	.140E-03	.228E-10	.8420E-25	.61E-04	.1833	22.8	6.39
.100E-11	.614E-17	.130E-02	.139E-03	.228E-10	.5040E-27	.52E-04	.1838	23.1	6.39
.100E-11	.630E-17	.129E-02	.138E-03	.228E-10	.2857E-29	.47E-04	.1834	23.3	6.39
.100E-11	.645E-17	.128E-02	.137E-03	.228E-10	.1522E-31	.40E-04	.1821	23.5	6.39

% NH3-N LOSS = .2357E-03, % UREA HYDROLYZED = 2.85
 % N ACCOUNT= 100.0, % C ACCOUNT= 100.3, % H ACCOUNT= 100.0, % CA ACCOUNT= 100.0

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
5.34	43.0	32.3	28.7	25.0	23.7	852.4	186.7	.01682	.00	.00	83.	45.

DAY	HOUR	MIN
181	12	0

NH4AQ	NH3C	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.340E-04	.238E-08	.955E-03	.886E-04	.213E-05	.2730E+01	.25E-01	.0148	42.9	6.56
.206E-04	.913E-09	.993E-03	.116E-03	.153E-05	.2908E-02	.12E-01	.0549	41.0	6.44
.419E-07	.125E-11	.103E-02	.140E-03	.256E-07	.6959E-04	.11E-02	.1137	38.8	6.36
.190E-10	.446E-15	.106E-02	.142E-03	.159E-09	.7714E-06	.39E-03	.1358	36.5	6.36
.103E-11	.198E-16	.110E-02	.143E-03	.233E-10	.2599E-08	.29E-03	.1491	34.5	6.36
.100E-11	.162E-16	.114E-02	.144E-03	.228E-10	.9112E-11	.22E-03	.1582	32.7	6.37
.100E-11	.139E-16	.118E-02	.145E-03	.228E-10	.4971E-13	.17E-03	.1648	31.2	6.37
.100E-11	.122E-16	.122E-02	.146E-03	.228E-10	.3951E-15	.14E-03	.1696	29.9	6.37
.100E-11	.109E-16	.125E-02	.147E-03	.228E-10	.3643E-17	.11E-03	.1732	28.7	6.38
.100E-11	.992E-17	.128E-02	.148E-03	.228E-10	.3416E-19	.88E-04	.1757	27.8	6.38
.100E-11	.918E-17	.131E-02	.148E-03	.228E-10	.3118E-21	.72E-04	.1773	27.0	6.38
.100E-11	.860E-17	.133E-02	.149E-03	.228E-10	.2731E-23	.59E-04	.1781	26.3	6.39
.100E-11	.816E-17	.134E-02	.149E-03	.228E-10	.2278E-25	.50E-04	.1782	25.8	6.39
.100E-11	.783E-17	.136E-02	.149E-03	.228E-10	.1792E-27	.47E-04	.1776	25.3	6.39
.100E-11	.756E-17	.136E-02	.148E-03	.228E-10	.1335E-29	.40E-04	.1764	25.0	6.39

% NH3-N LOSS = .1959E-01, % UREA HYDROLYZED = 5.01
 % N ACCOUNT= 100.0, % C ACCOUNT= 99.7, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.9

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOCV	RAIN	RA	RH
5.85	39.5	34.9	33.2	29.5	25.2	450.1	98.5	.01866	.00	.00	80.	43.

DAY	HR	MIN
181	18	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.340E-04	.229E-08	.565E-03	.500E-04	.213E-05	.2690E+01	.42E-01	.0150	42.2	6.57
.277E-04	.139E-08	.583E-03	.667E-04	.196E-05	.3627E-03	.29E-02	.0188	41.8	6.46
.129E-06	.484E-11	.597E-03	.861E-04	.538E-07	.2898E-06	.15E-02	.0830	41.3	6.35
.189E-09	.651E-14	.614E-03	.887E-04	.726E-09	.9547E-08	.45E-03	.1375	40.5	6.35
.150E-11	.473E-16	.633E-03	.900E-04	.298E-10	.5436E-09	.29E-03	.1512	39.7	6.35
.100E-11	.291E-16	.651E-03	.907E-04	.229E-10	.1610E-10	.22E-03	.1596	38.7	6.35
.100E-11	.265E-16	.669E-03	.910E-04	.228E-10	.2988E-12	.17E-03	.1654	37.7	6.36
.100E-11	.242E-16	.685E-03	.910E-04	.228E-10	.4053E-14	.14E-03	.1694	36.7	6.36
.100E-11	.220E-16	.700E-03	.908E-04	.228E-10	.4403E-16	.11E-03	.1723	35.6	6.37
.100E-11	.199E-16	.714E-03	.905E-04	.228E-10	.4284E-18	.88E-04	.1742	34.6	6.37
.100E-11	.181E-16	.726E-03	.899E-04	.228E-10	.4603E-20	.71E-04	.1753	33.5	6.38
.100E-11	.163E-16	.735E-03	.892E-04	.228E-10	.5393E-22	.59E-04	.1757	32.5	6.38
.100E-11	.148E-16	.743E-03	.884E-04	.228E-10	.6888E-24	.50E-04	.1756	31.4	6.38
.100E-11	.134E-16	.748E-03	.874E-04	.228E-10	.9730E-26	.46E-04	.1748	30.4	6.39
.100E-11	.121E-16	.750E-03	.862E-04	.228E-10	.6069E-28	.40E-04	.1736	29.5	6.39

% NH3-N LOSS = .1243E+00, % UREA HYDROLYZED = 5.61
 % N ACCOUNT= 100.0, % C ACCOUNT= 99.5, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.8

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOCV	RAIN	RA	RH
4.16	23.7	27.1	27.6	28.2	28.3	.1	.0	.01939	.00	.00	67.	50.

DAY	HR	MIN
182	0	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.387E-04	.548E-09	.722E-03	.499E-04	.232E-05	.1682E+01	.50E-01	.0239	26.5	6.59
.285E-04	.306E-09	.741E-03	.709E-04	.190E-05	.2734E-03	.28E-02	.0262	26.8	6.46
.133E-06	.116E-11	.755E-03	.934E-04	.550E-07	.2734E-06	.12E-02	.0876	27.3	6.35
.192E-09	.171E-14	.767E-03	.978E-04	.731E-09	.1191E-08	.42E-03	.1371	27.7	6.34
.151E-11	.140E-16	.779E-03	.991E-04	.299E-10	.2069E-10	.28E-03	.1487	28.1	6.34
.100E-11	.974E-17	.789E-03	.994E-04	.229E-10	.8209E-12	.21E-03	.1562	28.3	6.34
.100E-11	.101E-16	.795E-03	.991E-04	.228E-10	.2945E-13	.16E-03	.1616	28.5	6.35
.100E-11	.104E-16	.800E-03	.984E-04	.228E-10	.8288E-15	.13E-03	.1655	28.7	6.36
.100E-11	.106E-16	.803E-03	.975E-04	.228E-10	.1882E-16	.11E-03	.1683	28.8	6.36
.100E-11	.108E-16	.804E-03	.965E-04	.228E-10	.3572E-18	.86E-04	.1703	28.9	6.37
.100E-11	.108E-16	.804E-03	.954E-04	.228E-10	.5870E-20	.70E-04	.1715	28.7	6.37
.100E-11	.108E-16	.804E-03	.943E-04	.228E-10	.8804E-22	.58E-04	.1720	28.7	6.38
.100E-11	.108E-16	.804E-03	.932E-04	.228E-10	.1330E-23	.50E-04	.1720	28.5	6.38
.100E-11	.106E-16	.803E-03	.922E-04	.228E-10	.2443E-25	.45E-04	.1714	28.3	6.38
.100E-11	.105E-16	.803E-03	.914E-04	.228E-10	.3793E-27	.41E-04	.1701	28.2	6.39

% NH3-N LOSS = .1478E+00, % UREA HYDROLYZED = 5.94
 % N ACCOUNT= 100.0, % C ACCOUNT= 99.6, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.9

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOOV	RAIN	RA	RH
2.27	20.9	24.1	25.2	26.1	25.8	2.1	.5	.01803	.00	.00	125.	93.

DAY	HOUR	MIN
182	6	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.494E-04	.587E-09	.658E-03	.392E-04	.272E-05	.1554E+01	.61E-01	.0257	23.7	6.65
.298E-04	.236E-09	.671E-03	.626E-04	.196E-05	.3387E-03	.40E-02	.0296	24.1	6.45
.136E-06	.845E-12	.679E-03	.839E-04	.556E-07	.6632E-06	.10E-02	.1075	24.4	6.33
.193E-09	.121E-14	.687E-03	.877E-04	.734E-09	.3315E-08	.39E-03	.1354	24.8	6.32
.151E-11	.987E-17	.695E-03	.881E-04	.300E-10	.2464E-10	.26E-03	.1469	25.1	6.33
.100E-11	.684E-17	.701E-03	.878E-04	.229E-10	.2905E-12	.20E-03	.1542	25.3	6.33
.100E-11	.708E-17	.707E-03	.872E-04	.228E-10	.6869E-14	.16E-03	.1592	25.5	6.34
.100E-11	.733E-17	.712E-03	.865E-04	.228E-10	.2179E-15	.13E-03	.1628	25.7	6.35
.100E-11	.756E-17	.716E-03	.857E-04	.228E-10	.6495E-17	.10E-03	.1654	25.8	6.35
.100E-11	.777E-17	.720E-03	.849E-04	.228E-10	.1678E-18	.83E-04	.1672	25.9	6.36
.100E-11	.796E-17	.723E-03	.842E-04	.228E-10	.3756E-20	.69E-04	.1682	26.0	6.37
.100E-11	.811E-17	.725E-03	.835E-04	.228E-10	.7399E-22	.57E-04	.1687	26.1	6.37
.100E-11	.824E-17	.727E-03	.828E-04	.228E-10	.1313E-23	.49E-04	.1686	26.1	6.38
.100E-11	.834E-17	.728E-03	.822E-04	.228E-10	.2187E-25	.45E-04	.1679	26.1	6.38
.100E-11	.841E-17	.729E-03	.816E-04	.228E-10	.3569E-27	.41E-04	.1667	26.1	6.38

% NH3-N LOSS = .1713E+00, % UREA HYDROLYZED = 6.58
 % N ACCOUNT= 100.0, % C ACCOUNT= 99.6, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.9

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOOV	RAIN	RA	RH
5.38	45.7	33.0	30.4	27.0	25.4	837.4	186.9	.01878	.00	.00	82.	45.

DAY	HOUR	MIN
182	12	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.558E-04	.594E-08	.702E-03	.511E-04	.295E-05	.2724E+01	.68E-01	.0146	44.6	6.67
.315E-04	.168E-08	.721E-03	.842E-04	.203E-05	.3274E-03	.43E-02	.0185	42.6	6.45
.141E-06	.451E-11	.736E-03	.113E-03	.571E-07	.5537E-06	.95E-03	.1109	40.4	6.32
.195E-09	.485E-14	.752E-03	.116E-03	.740E-09	.6590E-08	.39E-03	.1367	38.2	6.31
.151E-11	.314E-16	.769E-03	.114E-03	.300E-10	.6416E-10	.26E-03	.1473	36.4	6.31
.100E-11	.180E-16	.785E-03	.112E-03	.229E-10	.5291E-12	.20E-03	.1540	34.7	6.32
.100E-11	.158E-16	.799E-03	.110E-03	.228E-10	.5097E-14	.16E-03	.1585	33.3	6.33
.100E-11	.141E-16	.812E-03	.108E-03	.228E-10	.7849E-16	.12E-03	.1617	32.0	6.34
.100E-11	.129E-16	.823E-03	.106E-03	.228E-10	.1950E-17	.10E-03	.1639	30.9	6.35
.100E-11	.119E-16	.833E-03	.104E-03	.228E-10	.5688E-19	.82E-04	.1654	30.0	6.35
.100E-11	.111E-16	.841E-03	.103E-03	.228E-10	.1578E-20	.68E-04	.1662	29.2	6.36
.100E-11	.105E-16	.847E-03	.101E-03	.228E-10	.3927E-22	.56E-04	.1665	28.6	6.37
.100E-11	.100E-16	.851E-03	.998E-04	.228E-10	.8827E-24	.49E-04	.1663	28.0	6.37
.100E-11	.957E-17	.854E-03	.985E-04	.228E-10	.1863E-25	.45E-04	.1655	27.5	6.38
.100E-11	.921E-17	.856E-03	.973E-04	.228E-10	.3105E-27	.41E-04	.1643	27.0	6.38

% NH3-N LOSS = .2297E+00, % UREA HYDROLYZED = 7.05
 % N ACCOUNT= 100.0, % C ACCOUNT= 99.6, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.8

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
6.31	40.6	35.7	34.3	30.6	26.5	440.1	97.9	.02025	.00	.00	76.	41.

DAY	HOUR	MIN
182	18	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.531E-04	.456E-08	.577E-03	.416E-04	.285E-05	.2599E+01	.69E-01	.0153	42.5	6.66
.318E-04	.164E-08	.592E-03	.691E-04	.204E-05	.2638E-03	.53E-03	.0194	42.3	6.45
.156E-06	.565E-11	.601E-03	.969E-04	.611E-07	.8517E-07	.91E-03	.0595	41.9	6.31
.200E-09	.659E-14	.611E-03	.100E-03	.754E-09	.3490E-09	.40E-03	.1333	41.3	6.30
.152E-11	.468E-16	.621E-03	.997E-04	.301E-10	.7124E-11	.27E-03	.1460	40.5	6.30
.100E-11	.290E-16	.631E-03	.982E-04	.229E-10	.2674E-12	.20E-03	.1536	39.6	6.31
.100E-11	.269E-16	.640E-03	.962E-04	.228E-10	.9704E-14	.16E-03	.1585	38.7	6.32
.100E-11	.249E-16	.648E-03	.940E-04	.228E-10	.3036E-15	.13E-03	.1617	37.7	6.33
.100E-11	.230E-16	.655E-03	.918E-04	.228E-10	.7930E-17	.10E-03	.1638	36.7	6.34
.100E-11	.211E-16	.661E-03	.896E-04	.228E-10	.1773E-18	.83E-04	.1651	35.7	6.35
.100E-11	.193E-16	.666E-03	.876E-04	.228E-10	.3567E-20	.68E-04	.1658	34.6	6.36
.100E-11	.177E-16	.670E-03	.856E-04	.228E-10	.7009E-22	.57E-04	.1659	33.6	6.36
.100E-11	.161E-16	.672E-03	.838E-04	.228E-10	.1494E-23	.49E-04	.1655	32.6	6.37
.100E-11	.147E-16	.674E-03	.820E-04	.228E-10	.3682E-25	.45E-04	.1647	31.6	6.38
.100E-11	.134E-16	.675E-03	.803E-04	.228E-10	.3721E-27	.41E-04	.1635	30.6	6.38

% NH3-N LOSS = .4687E+00, % UREA HYDROLYZED = 7.18
 % N ACCOUNT= 100.0, % C ACCOUNT= 99.5, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.8

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
4.57	25.1	28.0	29.2	29.4	27.4	.0	.0	.02094	.00	.00	60.	44.

DAY	HOUR	MIN
183	0	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.590E-04	.119E-08	.645E-03	.369E-04	.306E-05	.1679E+01	.76E-01	.0236	27.8	6.68
.327E-04	.401E-09	.667E-03	.656E-04	.208E-05	.2564E-03	.14E-02	.0263	28.2	6.45
.162E-06	.149E-11	.680E-03	.929E-04	.624E-07	.8229E-07	.79E-03	.0532	28.6	6.31
.202E-09	.183E-14	.692E-03	.100E-03	.758E-09	.2651E-09	.38E-03	.1362	28.9	6.29
.152E-11	.145E-16	.706E-03	.101E-03	.301E-10	.1765E-11	.25E-03	.1442	29.3	6.29
.100E-11	.101E-16	.718E-03	.101E-03	.229E-10	.1896E-13	.19E-03	.1503	29.6	6.30
.100E-11	.105E-16	.729E-03	.100E-03	.228E-10	.4642E-15	.15E-03	.1548	29.8	6.31
.100E-11	.110E-16	.738E-03	.990E-04	.228E-10	.1705E-16	.12E-03	.1581	29.9	6.32
.100E-11	.113E-16	.746E-03	.978E-04	.228E-10	.6270E-18	.10E-03	.1605	30.0	6.33
.100E-11	.116E-16	.753E-03	.966E-04	.228E-10	.2119E-19	.82E-04	.1621	30.0	6.34
.100E-11	.118E-16	.758E-03	.953E-04	.228E-10	.6675E-21	.67E-04	.1631	30.0	6.35
.100E-11	.119E-16	.762E-03	.941E-04	.228E-10	.2031E-22	.56E-04	.1635	29.9	6.36
.100E-11	.119E-16	.765E-03	.929E-04	.228E-10	.6260E-24	.49E-04	.1633	29.7	6.37
.100E-11	.118E-16	.767E-03	.917E-04	.228E-10	.2103E-25	.44E-04	.1626	29.6	6.37
.100E-11	.117E-16	.768E-03	.906E-04	.228E-10	.3981E-27	.41E-04	.1615	29.4	6.38

% NH3-N LOSS = .5277E+00, % UREA HYDROLYZED = 7.58
 % N ACCOUNT= 100.0, % C ACCOUNT= 99.5, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.8

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
2.46	20.4	23.2	25.1	27.4	26.9	2.2	.5	.01734	.00	.00	114.	85.

DAY	HOUR	MIN
183	6	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.751E-04	.991E-09	.841E-03	.406E-04	.359E-05	.1445E+01	.88E-01	.0272	22.9	6.73
.341E-04	.245E-09	.854E-03	.800E-04	.214E-05	.3525E-03	.26E-02	.0304	23.3	6.45
.164E-06	.886E-12	.860E-03	.113E-03	.630E-07	.2071E-06	.66E-03	.0658	23.8	6.30
.203E-09	.108E-14	.865E-03	.122E-03	.760E-09	.7735E-09	.36E-03	.1353	24.3	6.27
.152E-11	.871E-17	.868E-03	.121E-03	.301E-10	.5299E-11	.25E-03	.1435	24.8	6.28
.100E-11	.620E-17	.870E-03	.119E-03	.229E-10	.4040E-13	.19E-03	.1490	25.2	6.29
.100E-11	.663E-17	.871E-03	.116E-03	.228E-10	.3599E-15	.15E-03	.1530	25.6	6.30
.100E-11	.708E-17	.871E-03	.114E-03	.228E-10	.4861E-17	.12E-03	.1561	26.0	6.32
.100E-11	.751E-17	.870E-03	.111E-03	.228E-10	.1197E-18	.97E-04	.1582	26.3	6.33
.100E-11	.792E-17	.868E-03	.108E-03	.228E-10	.3925E-20	.80E-04	.1597	26.5	6.34
.100E-11	.830E-17	.867E-03	.106E-03	.228E-10	.1312E-21	.66E-04	.1607	26.8	6.35
.100E-11	.864E-17	.865E-03	.104E-03	.228E-10	.4195E-23	.56E-04	.1610	27.0	6.36
.100E-11	.895E-17	.863E-03	.103E-03	.228E-10	.1299E-24	.48E-04	.1608	27.1	6.36
.100E-11	.921E-17	.862E-03	.101E-03	.228E-10	.4044E-26	.44E-04	.1602	27.3	6.37
.100E-11	.943E-17	.862E-03	.999E-04	.228E-10	.1108E-27	.41E-04	.1590	27.4	6.38

% NH3-N LOSS = .5632E+00, % UREA HYDROLYZED = 8.40

% N ACCOUNT= 100.0, % C ACCOUNT= 99.6, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.9

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
7.16	43.8	31.4	30.3	27.6	26.3	830.0	188.7	.01989	.00	.00	66.	36.

DAY	HOUR	MIN
183	12	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.809E-04	.791E-08	.791E-03	.461E-04	.378E-05	.2534E+01	.93E-01	.0154	41.8	6.75
.360E-04	.149E-08	.814E-03	.931E-04	.221E-05	.2621E-03	.35E-02	.0203	40.1	6.45
.168E-06	.416E-11	.829E-03	.132E-03	.641E-07	.1732E-06	.60E-03	.0730	38.5	6.30
.204E-09	.395E-14	.845E-03	.142E-03	.763E-09	.8564E-09	.35E-03	.1314	36.8	6.26
.152E-11	.254E-16	.862E-03	.139E-03	.301E-10	.9341E-11	.24E-03	.1426	35.2	6.27
.100E-11	.150E-16	.879E-03	.136E-03	.229E-10	.9466E-13	.19E-03	.1487	33.8	6.28
.100E-11	.136E-16	.895E-03	.132E-03	.228E-10	.8836E-15	.15E-03	.1527	32.6	6.30
.100E-11	.126E-16	.909E-03	.128E-03	.228E-10	.8243E-17	.12E-03	.1554	31.5	6.31
.100E-11	.118E-16	.922E-03	.125E-03	.228E-10	.8805E-19	.96E-04	.1573	30.7	6.32
.100E-11	.112E-16	.933E-03	.123E-03	.228E-10	.1360E-20	.79E-04	.1585	29.9	6.33
.100E-11	.107E-16	.942E-03	.120E-03	.228E-10	.3324E-22	.65E-04	.1592	29.3	6.34
.100E-11	.103E-16	.949E-03	.118E-03	.228E-10	.1016E-23	.55E-04	.1594	28.7	6.35
.100E-11	.100E-16	.955E-03	.116E-03	.228E-10	.3226E-25	.48E-04	.1591	28.3	6.36
.100E-11	.977E-17	.959E-03	.114E-03	.228E-10	.1025E-26	.44E-04	.1584	27.9	6.37
.100E-11	.955E-17	.961E-03	.112E-03	.228E-10	.2866E-28	.41E-04	.1573	27.6	6.37

% NH3-N LOSS = .6679E+00, % UREA HYDROLYZED = 8.86

% N ACCOUNT= 100.0, % C ACCOUNT= 99.5, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.7

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOOV	RAIN	RA	RH
6.33	34.9	32.6	33.5	30.5	27.1	229.2	51.4	.02141	.00	.00	79.	41.

DAY	HOUR	MIN
183	18	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.743E-04	.448E-08	.648E-03	.381E-04	.357E-05	.2304E+01	.89E-01	.0169	37.5	6.72
.366E-04	.123E-08	.664E-03	.740E-04	.224E-05	.2444E-03	.74E-03	.0199	38.0	6.45
.182E-06	.439E-11	.672E-03	.108E-03	.676E-07	.2212E-07	.59E-03	.0296	38.3	6.29
.209E-09	.465E-14	.680E-03	.119E-03	.772E-09	.8599E-10	.34E-03	.1284	38.4	6.25
.152E-11	.342E-16	.689E-03	.118E-03	.301E-10	.1551E-11	.24E-03	.1404	38.3	6.26
.100E-11	.224E-16	.697E-03	.115E-03	.229E-10	.4283E-13	.19E-03	.1476	37.9	6.28
.100E-11	.218E-16	.705E-03	.112E-03	.228E-10	.1264E-14	.15E-03	.1523	37.3	6.29
.100E-11	.209E-16	.712E-03	.109E-03	.228E-10	.3492E-16	.12E-03	.1553	36.6	6.30
.100E-11	.199E-16	.718E-03	.105E-03	.228E-10	.8588E-18	.97E-04	.1573	35.8	6.32
.100E-11	.188E-16	.723E-03	.102E-03	.228E-10	.1824E-19	.80E-04	.1585	35.0	6.33
.100E-11	.176E-16	.728E-03	.990E-04	.228E-10	.3387E-21	.66E-04	.1590	34.1	6.34
.100E-11	.164E-16	.731E-03	.963E-04	.228E-10	.5653E-23	.55E-04	.1591	33.2	6.35
.100E-11	.152E-16	.734E-03	.937E-04	.228E-10	.8963E-25	.48E-04	.1587	32.3	6.36
.100E-11	.141E-16	.735E-03	.914E-04	.228E-10	.1512E-26	.44E-04	.1579	31.4	6.36
.100E-11	.130E-16	.736E-03	.893E-04	.228E-10	.1222E-28	.41E-04	.1568	30.5	6.37

% NH3-N LOSS = .1034E+01, % UREA HYDROLYZED = 8.99
 % N ACCOUNT= 100.0, % C ACCOUNT= 99.5, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.8

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOOV	RAIN	RA	RH
5.01	25.5	28.1	29.2	29.3	27.8	.0	.0	.02106	.00	.00	55.	41.

DAY	HOUR	MIN
184	0	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.819E-04	.184E-08	.753E-03	.378E-04	.381E-05	.1596E+01	.96E-01	.0243	27.6	6.74
.376E-04	.443E-09	.775E-03	.769E-04	.228E-05	.2835E-03	.15E-02	.0251	28.0	6.45
.187E-06	.159E-11	.786E-03	.112E-03	.688E-07	.4104E-07	.53E-03	.0304	28.3	6.29
.210E-09	.166E-14	.796E-03	.127E-03	.776E-09	.1174E-09	.33E-03	.1312	28.6	6.24
.152E-11	.127E-16	.808E-03	.126E-03	.301E-10	.6923E-12	.23E-03	.1389	28.9	6.25
.100E-11	.889E-17	.817E-03	.124E-03	.229E-10	.5801E-14	.18E-03	.1448	29.1	6.27
.100E-11	.936E-17	.826E-03	.121E-03	.228E-10	.9680E-16	.14E-03	.1492	29.3	6.28
.100E-11	.983E-17	.832E-03	.118E-03	.228E-10	.2650E-17	.12E-03	.1523	29.5	6.30
.100E-11	.103E-16	.839E-03	.115E-03	.228E-10	.7948E-19	.95E-04	.1545	29.6	6.31
.100E-11	.106E-16	.842E-03	.113E-03	.228E-10	.2271E-20	.79E-04	.1560	29.6	6.32
.100E-11	.109E-16	.845E-03	.110E-03	.228E-10	.6113E-22	.65E-04	.1568	29.6	6.34
.100E-11	.111E-16	.848E-03	.108E-03	.228E-10	.1587E-23	.55E-04	.1571	29.6	6.35
.100E-11	.113E-16	.849E-03	.106E-03	.228E-10	.4088E-25	.48E-04	.1569	29.5	6.35
.100E-11	.114E-16	.850E-03	.104E-03	.228E-10	.1101E-26	.44E-04	.1563	29.4	6.36
.100E-11	.114E-16	.851E-03	.102E-03	.228E-10	.1812E-28	.41E-04	.1551	29.3	6.37

% NH3-N LOSS = .1115E+01, % UREA HYDROLYZED = 9.44
 % N ACCOUNT= 100.0, % C ACCOUNT= 99.5, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.8

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
6.99	23.7	26.6	27.0	27.7	27.3	2.6	.6	.01857	.00	.00	39.	29.

DAY	HOUR	MIN
184	6	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.964E-04	.189E-08	.679E-03	.309E-04	.424E-05	.1601E+01	.10E+00	.0240	25.7	6.77
.389E-04	.366E-09	.705E-03	.686E-04	.233E-05	.3192E-03	.25E-02	.0274	25.9	6.44
.190E-06	.126E-11	.719E-03	.101E-03	.695E-07	.6838E-07	.49E-03	.0365	26.0	6.29
.211E-09	.127E-14	.731E-03	.116E-03	.779E-09	.2534E-09	.32E-03	.1333	26.2	6.23
.152E-11	.961E-17	.744E-03	.116E-03	.301E-10	.1795E-11	.23E-03	.1393	26.5	6.24
.100E-11	.670E-17	.757E-03	.114E-03	.229E-10	.1336E-13	.18E-03	.1441	26.7	6.26
.100E-11	.707E-17	.767E-03	.111E-03	.228E-10	.1079E-15	.14E-03	.1478	26.9	6.27
.100E-11	.746E-17	.776E-03	.109E-03	.228E-10	.1107E-17	.11E-03	.1507	27.0	6.29
.100E-11	.785E-17	.784E-03	.107E-03	.228E-10	.1832E-19	.94E-04	.1527	27.2	6.31
.100E-11	.821E-17	.790E-03	.104E-03	.228E-10	.4483E-21	.77E-04	.1541	27.3	6.32
.100E-11	.855E-17	.795E-03	.102E-03	.228E-10	.1228E-22	.64E-04	.1549	27.4	6.33
.100E-11	.886E-17	.799E-03	.100E-03	.228E-10	.3321E-24	.54E-04	.1552	27.5	6.34
.100E-11	.914E-17	.802E-03	.984E-04	.228E-10	.8681E-26	.48E-04	.1551	27.6	6.35
.100E-11	.937E-17	.804E-03	.968E-04	.228E-10	.2234E-27	.44E-04	.1544	27.7	6.36
.100E-11	.957E-17	.805E-03	.954E-04	.228E-10	.5147E-29	.41E-04	.1533	27.7	6.37

% NH3-N LOSS = .1207E+01, % UREA HYDROLYZED = 10.20

% N ACCOUNT= 100.0, % C ACCOUNT= 99.6, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.8

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
8.50	45.0	34.4	31.2	28.2	26.8	849.0	194.9	.01765	.00	.00	58.	31.

DAY	HOUR	MIN
184	12	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.967E-04	.118E-07	.681E-03	.401E-04	.425E-05	.2658E+01	.98E-01	.0144	43.9	6.76
.403E-04	.204E-08	.700E-03	.833E-04	.239E-05	.3125E-03	.23E-02	.0184	42.3	6.44
.196E-06	.592E-11	.710E-03	.120E-03	.710E-07	.2896E-07	.47E-03	.0287	40.8	6.28
.212E-09	.474E-14	.720E-03	.137E-03	.783E-09	.2049E-09	.31E-03	.1306	39.1	6.22
.152E-11	.295E-16	.733E-03	.132E-03	.301E-10	.4009E-11	.23E-03	.1400	37.4	6.23
.100E-11	.173E-16	.744E-03	.127E-03	.229E-10	.5912E-13	.18E-03	.1450	35.9	6.25
.100E-11	.156E-16	.755E-03	.122E-03	.228E-10	.6279E-15	.14E-03	.1483	34.5	6.27
.100E-11	.143E-16	.764E-03	.117E-03	.228E-10	.5161E-17	.11E-03	.1507	33.4	6.28
.100E-11	.133E-16	.772E-03	.113E-03	.228E-10	.3820E-19	.93E-04	.1523	32.3	6.30
.100E-11	.125E-16	.779E-03	.109E-03	.228E-10	.3258E-21	.77E-04	.1534	31.4	6.31
.100E-11	.119E-16	.785E-03	.105E-03	.228E-10	.4296E-23	.64E-04	.1540	30.6	6.33
.100E-11	.113E-16	.790E-03	.102E-03	.228E-10	.8945E-25	.54E-04	.1542	29.9	6.34
.100E-11	.108E-16	.793E-03	.998E-04	.228E-10	.2294E-26	.47E-04	.1539	29.3	6.35
.100E-11	.104E-16	.795E-03	.975E-04	.228E-10	.6199E-28	.44E-04	.1531	28.7	6.36
.100E-11	.100E-16	.796E-03	.954E-04	.228E-10	.1307E-29	.41E-04	.1520	28.2	6.36

% NH3-N LOSS = .1421E+01, % UREA HYDROLYZED = 10.50

% N ACCOUNT= 100.0, % C ACCOUNT= 99.5, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.7

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
3.67	43.8	36.9	34.3	30.8	27.4	485.8	111.8	.01488	.00	.00	113.	62.

DAY	HOUR	MIN
184	18	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.859E-04	.112E-07	.646E-03	.434E-04	.393E-05	.2804E+01	.88E-01	.0137	45.7	6.71
.407E-04	.266E-08	.656E-03	.814E-04	.240E-05	.3779E-03	.72E-03	.0160	45.0	6.44
.218E-06	.917E-11	.661E-03	.117E-03	.762E-07	.3003E-07	.21E-03	.0197	44.2	6.28
.218E-09	.717E-14	.665E-03	.135E-03	.797E-09	.3054E-10	.29E-03	.0990	43.2	6.22
.152E-11	.458E-16	.669E-03	.130E-03	.302E-10	.1516E-12	.22E-03	.1335	42.0	6.23
.100E-11	.280E-16	.672E-03	.124E-03	.229E-10	.5066E-14	.18E-03	.1434	40.9	6.24
.100E-11	.259E-16	.675E-03	.118E-03	.228E-10	.2894E-15	.14E-03	.1484	39.7	6.26
.100E-11	.240E-16	.678E-03	.112E-03	.228E-10	.1490E-16	.12E-03	.1513	38.6	6.28
.100E-11	.222E-16	.680E-03	.107E-03	.228E-10	.6103E-18	.95E-04	.1531	37.4	6.29
.100E-11	.206E-16	.681E-03	.102E-03	.228E-10	.1984E-19	.78E-04	.1540	36.3	6.31
.100E-11	.189E-16	.682E-03	.977E-04	.228E-10	.5234E-21	.65E-04	.1544	35.2	6.32
.100E-11	.174E-16	.683E-03	.938E-04	.228E-10	.1148E-22	.55E-04	.1544	34.1	6.34
.100E-11	.159E-16	.683E-03	.904E-04	.228E-10	.2143E-24	.48E-04	.1540	33.0	6.35
.100E-11	.145E-16	.683E-03	.873E-04	.228E-10	.3478E-26	.44E-04	.1532	31.9	6.36
.100E-11	.131E-16	.683E-03	.847E-04	.228E-10	.1412E-28	.41E-04	.1520	30.8	6.36

% NH3-N LOSS = .1955E+01, % UREA HYDROLYZED = 10.63

% N ACCOUNT= 100.0, % C ACCOUNT= 99.5, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.7

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
2.95	21.1	23.4	29.5	30.1	28.3	.1	.0	.01782	.02	.00	162.	87.

DAY	HOUR	MIN
185	0	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.880E-04	.139E-08	.920E-03	.474E-04	.399E-05	.1650E+01	.90E-01	.0231	24.9	6.72
.411E-04	.375E-09	.929E-03	.910E-04	.242E-05	.3872E-03	.83E-03	.0223	25.7	6.44
.228E-06	.156E-11	.932E-03	.133E-03	.784E-07	.5039E-07	.27E-03	.0253	26.4	6.28
.221E-09	.140E-14	.933E-03	.158E-03	.805E-09	.5574E-10	.26E-03	.0929	27.2	6.21
.152E-11	.108E-16	.933E-03	.156E-03	.302E-10	.1738E-12	.21E-03	.1281	28.0	6.22
.100E-11	.794E-17	.932E-03	.151E-03	.229E-10	.8675E-15	.17E-03	.1382	28.7	6.24
.100E-11	.874E-17	.930E-03	.145E-03	.228E-10	.9053E-17	.14E-03	.1440	29.3	6.25
.100E-11	.953E-17	.927E-03	.140E-03	.228E-10	.3748E-18	.11E-03	.1478	29.7	6.27
.100E-11	.102E-16	.924E-03	.134E-03	.228E-10	.2264E-19	.94E-04	.1502	30.0	6.29
.100E-11	.109E-16	.921E-03	.129E-03	.228E-10	.1242E-20	.78E-04	.1518	30.2	6.31
.100E-11	.114E-16	.917E-03	.125E-03	.228E-10	.5850E-22	.65E-04	.1526	30.4	6.32
.100E-11	.118E-16	.915E-03	.121E-03	.228E-10	.2526E-23	.55E-04	.1529	30.4	6.33
.100E-11	.120E-16	.912E-03	.118E-03	.228E-10	.9686E-25	.48E-04	.1528	30.4	6.34
.100E-11	.122E-16	.910E-03	.115E-03	.228E-10	.3439E-26	.44E-04	.1521	30.3	6.35
.100E-11	.122E-16	.909E-03	.112E-03	.228E-10	.5180E-28	.41E-04	.1510	30.1	6.36

% NH3-N LOSS = .2051E+01, % UREA HYDROLYZED = 10.84

% N ACCOUNT= 100.0, % C ACCOUNT= 99.5, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.8

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
2.24	20.0	19.8	25.7	27.5	27.7	.5	.1	.01290	.75	.00	204.	110.

DAY	HOUR	MIN
185	6	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.947E-04	.104E-08	.118E-02	.555E-04	.419E-05	.1781E+01	.95E-01	.0214	21.1	6.74
.421E-04	.245E-09	.119E-02	.113E-03	.246E-05	.4005E-03	.16E-02	.0234	21.6	6.44
.230E-06	.979E-12	.120E-02	.164E-03	.789E-07	.7501E-07	.36E-03	.0289	22.1	6.28
.222E-09	.848E-15	.120E-02	.196E-03	.807E-09	.1483E-09	.25E-03	.1042	22.7	6.20
.152E-11	.636E-17	.120E-02	.194E-03	.302E-10	.6725E-12	.20E-03	.1263	23.3	6.21
.100E-11	.465E-17	.120E-02	.187E-03	.229E-10	.3942E-14	.17E-03	.1360	23.9	6.23
.100E-11	.514E-17	.119E-02	.180E-03	.228E-10	.2547E-16	.14E-03	.1418	24.5	6.25
.100E-11	.567E-17	.119E-02	.173E-03	.228E-10	.1996E-18	.11E-03	.1456	25.0	6.27
.100E-11	.622E-17	.119E-02	.166E-03	.228E-10	.3475E-20	.92E-04	.1481	25.5	6.28
.100E-11	.678E-17	.119E-02	.160E-03	.228E-10	.1439E-21	.76E-04	.1498	25.9	6.30
.100E-11	.732E-17	.118E-02	.155E-03	.228E-10	.6842E-23	.64E-04	.1507	26.3	6.32
.100E-11	.785E-17	.118E-02	.151E-03	.228E-10	.2985E-24	.54E-04	.1511	26.7	6.33
.100E-11	.834E-17	.118E-02	.147E-03	.228E-10	.1174E-25	.47E-04	.1509	27.0	6.34
.100E-11	.881E-17	.117E-02	.144E-03	.228E-10	.4211E-27	.43E-04	.1503	27.3	6.35
.100E-11	.923E-17	.117E-02	.141E-03	.228E-10	.1115E-28	.41E-04	.1492	27.5	6.36

% NH3-N LOSS = .2070E+01, % UREA HYDROLYZED = 11.17

% N ACCOUNT= 100.0, % C ACCOUNT= 99.6, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.8

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
1.53	35.5	23.7	26.9	26.2	26.7	669.4	145.8	.01251	.88	.00	193.	111.

DAY	HOUR	MIN
185	12	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.117E-03	.610E-08	.157E-02	.753E-04	.481E-05	.2020E+01	.99E-01	.0174	34.5	6.79
.525E-04	.990E-09	.158E-02	.162E-03	.284E-05	.8544E-01	.21E-01	.0273	32.2	6.45
.263E-06	.275E-11	.159E-02	.240E-03	.862E-07	.2555E-03	.62E-03	.0322	30.5	6.28
.226E-09	.168E-14	.159E-02	.283E-03	.816E-09	.1629E-06	.24E-03	.1116	29.0	6.20
.152E-11	.103E-16	.159E-02	.275E-03	.302E-10	.1776E-09	.20E-03	.1264	27.9	6.20
.100E-11	.650E-17	.159E-02	.262E-03	.229E-10	.2522E-12	.16E-03	.1350	27.2	6.22
.100E-11	.643E-17	.159E-02	.249E-03	.228E-10	.4849E-15	.13E-03	.1405	26.7	6.24
.100E-11	.649E-17	.159E-02	.237E-03	.228E-10	.1384E-17	.11E-03	.1442	26.4	6.26
.100E-11	.661E-17	.158E-02	.226E-03	.228E-10	.6481E-20	.90E-04	.1467	26.1	6.28
.100E-11	.679E-17	.158E-02	.216E-03	.228E-10	.5924E-22	.75E-04	.1484	26.0	6.30
.100E-11	.699E-17	.158E-02	.208E-03	.228E-10	.1376E-23	.63E-04	.1493	26.0	6.31
.100E-11	.722E-17	.157E-02	.201E-03	.228E-10	.5230E-25	.54E-04	.1497	26.0	6.33
.100E-11	.747E-17	.157E-02	.196E-03	.228E-10	.2046E-26	.47E-04	.1495	26.0	6.34
.100E-11	.772E-17	.157E-02	.191E-03	.228E-10	.7388E-28	.43E-04	.1489	26.1	6.35
.100E-11	.797E-17	.157E-02	.187E-03	.228E-10	.2280E-29	.41E-04	.1478	26.2	6.36

% NH3-N LOSS = .2091E+01, % UREA HYDROLYZED = 12.56

% N ACCOUNT= 100.0, % C ACCOUNT= 99.6, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.7

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
2.25	38.8	28.8	33.4	29.8	27.0	469.1	102.0	.01120	.16	.00	149.	84.

DAY	HOURL	MIN
185	18	0

NH4AQ	NH3G	HC03	CO2G	NH4AD	UREA	CA	WA	TA	PH
.110E-03	.111E-07	.129E-02	.704E-04	.462E-05	.2718E+01	.10E+00	.0136	41.5	6.78
.588E-04	.279E-08	.131E-02	.147E-03	.306E-05	.1793E-01	.47E-02	.0160	41.2	6.46
.443E-06	.131E-10	.132E-02	.226E-03	.122E-06	.3008E-05	.46E-03	.0199	40.8	6.28
.627E-09	.145E-13	.132E-02	.275E-03	.160E-08	.5268E-08	.24E-03	.0819	40.2	6.19
.320E-11	.698E-16	.133E-02	.269E-03	.492E-10	.7390E-09	.20E-03	.1248	39.5	6.20
.104E-11	.216E-16	.134E-02	.257E-03	.234E-10	.7465E-10	.17E-03	.1355	38.6	6.22
.100E-11	.200E-16	.135E-02	.244E-03	.229E-10	.4635E-11	.14E-03	.1415	37.7	6.24
.100E-11	.191E-16	.136E-02	.232E-03	.228E-10	.1977E-12	.11E-03	.1452	36.8	6.26
.100E-11	.181E-16	.136E-02	.220E-03	.228E-10	.6170E-14	.92E-04	.1476	35.9	6.27
.100E-11	.171E-16	.137E-02	.210E-03	.228E-10	.1475E-15	.76E-04	.1490	34.9	6.29
.100E-11	.160E-16	.138E-02	.201E-03	.228E-10	.2792E-17	.64E-04	.1497	33.9	6.31
.100E-11	.149E-16	.138E-02	.193E-03	.228E-10	.4298E-19	.54E-04	.1499	32.9	6.32
.100E-11	.138E-16	.138E-02	.185E-03	.228E-10	.5495E-21	.47E-04	.1496	31.9	6.34
.100E-11	.127E-16	.139E-02	.179E-03	.228E-10	.5938E-23	.43E-04	.1488	30.8	6.35
.100E-11	.117E-16	.139E-02	.173E-03	.228E-10	.1552E-25	.41E-04	.1477	29.8	6.36

% NH3-N LOSS = .2430E+01, % UREA HYDROLYZED = 13.00
 % N ACCOUNT= 100.0, % C ACCOUNT= 99.4, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.6

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
.51	15.7	17.1	26.5	28.3	27.6	.0	.0	.01249	.00	.00	472.	280.

DAY	HOURL	MIN
186	0	0

NH4AQ	NH3G	HC03	CO2G	NH4AD	UREA	CA	WA	TA	PH
.111E-03	.120E-08	.170E-02	.720E-04	.464E-05	.1778E+01	.10E+00	.0209	20.2	6.78
.605E-04	.353E-09	.171E-02	.152E-03	.312E-05	.4435E-02	.36E-02	.0212	21.1	6.46
.454E-06	.189E-11	.171E-02	.236E-03	.124E-06	.8338E-06	.34E-03	.0246	22.1	6.27
.633E-09	.239E-14	.170E-02	.292E-03	.161E-08	.9025E-09	.23E-03	.0775	23.0	6.19
.322E-11	.137E-16	.170E-02	.290E-03	.494E-10	.1571E-10	.19E-03	.1229	24.0	6.19
.104E-11	.508E-17	.169E-02	.290E-03	.234E-10	.1734E-11	.16E-03	.1324	24.9	6.21
.100E-11	.559E-17	.169E-02	.268E-03	.229E-10	.1416E-12	.13E-03	.1382	25.6	6.23
.100E-11	.629E-17	.168E-02	.257E-03	.228E-10	.8323E-14	.11E-03	.1422	26.3	6.25
.100E-11	.697E-17	.167E-02	.246E-03	.228E-10	.3821E-15	.91E-04	.1449	26.8	6.27
.100E-11	.762E-17	.167E-02	.236E-03	.228E-10	.1453E-16	.76E-04	.1466	27.3	6.29
.100E-11	.821E-17	.166E-02	.227E-03	.228E-10	.4771E-18	.63E-04	.1477	27.6	6.30
.100E-11	.874E-17	.166E-02	.219E-03	.228E-10	.1398E-19	.54E-04	.1481	27.9	6.32
.100E-11	.918E-17	.165E-02	.213E-03	.228E-10	.3747E-21	.47E-04	.1481	28.1	6.33
.100E-11	.955E-17	.165E-02	.207E-03	.228E-10	.9423E-23	.43E-04	.1475	28.2	6.34
.100E-11	.984E-17	.165E-02	.202E-03	.228E-10	.1324E-24	.42E-04	.1464	28.3	6.35

% NH3-N LOSS = .2479E+01, % UREA HYDROLYZED = 13.17
 % N ACCOUNT= 100.0, % C ACCOUNT= 99.5, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.7

UHM TSURF TAIR T6CM T15CM T30CM SW RESW VDA CLDOOV RAIN RA RH
 .69 14.2 16.5 22.8 25.4 26.6 3.1 .7 .01220 .00 .00 117761. 1000.

DAY HOUR MIN
 186 6 0

NH4AQ	NH3G	HC03	CO2G	NH4AD	UREA	CA	WA	TA	PH
.118E-03	.795E-09	.223E-02	.864E-04	.485E-05	.1447E+01	.10E+00	.0256	15.6	6.80
.635E-04	.212E-09	.223E-02	.188E-03	.322E-05	.1732E-02	.54E-02	.0246	16.3	6.46
.457E-06	.106E-11	.222E-02	.295E-03	.124E-06	.5603E-06	.39E-03	.0280	16.9	6.27
.635E-09	.131E-14	.222E-02	.365E-03	.161E-08	.1046E-08	.22E-03	.0873	17.7	6.18
.322E-11	.743E-17	.221E-02	.364E-03	.494E-10	.7332E-11	.19E-03	.1216	18.6	6.18
.104E-11	.275E-17	.220E-02	.350E-03	.234E-10	.3127E-12	.16E-03	.1312	19.5	6.20
.100E-11	.305E-17	.219E-02	.335E-03	.229E-10	.2416E-13	.13E-03	.1369	20.3	6.22
.100E-11	.349E-17	.218E-02	.320E-03	.228E-10	.1493E-14	.11E-03	.1407	21.1	6.24
.100E-11	.397E-17	.217E-02	.306E-03	.228E-10	.7276E-16	.89E-04	.1433	21.8	6.27
.100E-11	.448E-17	.216E-02	.294E-03	.228E-10	.2929E-17	.74E-04	.1450	22.5	6.28
.100E-11	.501E-17	.216E-02	.283E-03	.228E-10	.1010E-18	.62E-04	.1461	23.1	6.30
.100E-11	.555E-17	.215E-02	.274E-03	.228E-10	.3072E-20	.53E-04	.1465	23.7	6.32
.100E-11	.610E-17	.214E-02	.267E-03	.228E-10	.8408E-22	.47E-04	.1465	24.3	6.33
.100E-11	.666E-17	.214E-02	.261E-03	.228E-10	.2110E-23	.42E-04	.1459	24.9	6.34
.100E-11	.721E-17	.214E-02	.256E-03	.228E-10	.4393E-25	.42E-04	.1448	25.4	6.35

% NH3-N LOSS = .2483E+01, % UREA HYDROLYZED = 13.59

% N ACCOUNT= 100.0, % C ACCOUNT= 99.7, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.7

UHM TSURF TAIR T6CM T15CM T30CM SW RESW VDA CLDOOV RAIN RA RH
 2.19 48.2 26.4 29.6 26.0 25.7 881.3 195.1 .01151 .00 .00 142. 81.

DAY HOUR MIN
 186 12 0

NH4AQ	NH3G	HC03	CO2G	NH4AD	UREA	CA	WA	TA	PH
.122E-03	.181E-07	.209E-02	.108E-03	.496E-05	.2724E+01	.10E+00	.0135	44.5	6.82
.704E-04	.382E-08	.212E-02	.236E-03	.345E-05	.6237E-02	.79E-02	.0170	42.3	6.47
.469E-06	.131E-10	.213E-02	.370E-03	.126E-06	.7116E-06	.45E-03	.0230	40.3	6.27
.639E-09	.116E-13	.215E-02	.449E-03	.162E-08	.1339E-08	.21E-03	.0903	38.2	6.17
.322E-11	.467E-16	.216E-02	.438E-03	.494E-10	.2334E-10	.18E-03	.1210	35.9	6.18
.104E-11	.130E-16	.218E-02	.413E-03	.234E-10	.2818E-12	.15E-03	.1312	34.0	6.20
.100E-11	.111E-16	.220E-02	.388E-03	.229E-10	.5077E-14	.13E-03	.1370	32.4	6.22
.100E-11	.101E-16	.221E-02	.366E-03	.228E-10	.2536E-15	.11E-03	.1407	31.0	6.24
.100E-11	.939E-17	.223E-02	.346E-03	.228E-10	.1392E-16	.88E-04	.1431	29.8	6.26
.100E-11	.886E-17	.224E-02	.329E-03	.228E-10	.6338E-18	.74E-04	.1446	28.9	6.28
.100E-11	.847E-17	.225E-02	.315E-03	.228E-10	.2425E-19	.62E-04	.1455	28.1	6.30
.100E-11	.818E-17	.226E-02	.303E-03	.228E-10	.8028E-21	.53E-04	.1458	27.4	6.31
.100E-11	.797E-17	.227E-02	.292E-03	.228E-10	.2357E-22	.46E-04	.1456	26.8	6.33
.100E-11	.781E-17	.228E-02	.284E-03	.228E-10	.6256E-24	.42E-04	.1450	26.4	6.34
.100E-11	.768E-17	.228E-02	.276E-03	.228E-10	.1359E-25	.42E-04	.1439	26.0	6.35

% NH3-N LOSS = .2566E+01, % UREA HYDROLYZED = 14.13

% N ACCOUNT= 100.0, % C ACCOUNT= 99.5, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.6

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
1.56	40.6	28.6	34.5	30.1	26.7	469.5	102.9	.01123	.00	.00	181.	105.

DAY	HOUR	MIN
196	18	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.114E-03	.142E-07	.171E-02	.904E-04	.473E-05	.2711E+01	.99E-01	.0135	43.1	6.80
.715E-04	.410E-09	.173E-02	.195E-03	.349E-05	.5362E-03	.11E-02	.0161	42.9	6.47
.529E-06	.184E-10	.174E-02	.312E-03	.137E-06	.5410E-07	.18E-03	.0201	42.6	6.27
.662E-09	.177E-13	.175E-02	.389E-03	.166E-08	.8747E-11	.18E-03	.0400	42.1	6.17
.322E-11	.807E-16	.175E-02	.386E-03	.494E-10	.1893E-12	.18E-03	.1165	41.5	6.17
.104E-11	.248E-16	.176E-02	.367E-03	.234E-10	.1752E-13	.16E-03	.1304	40.6	6.19
.100E-11	.228E-16	.177E-02	.346E-03	.229E-10	.1537E-14	.13E-03	.1375	39.6	6.21
.100E-11	.215E-16	.178E-02	.326E-03	.228E-10	.1039E-15	.11E-03	.1417	38.5	6.23
.100E-11	.201E-16	.178E-02	.307E-03	.228E-10	.5480E-17	.91E-04	.1443	37.3	6.26
.100E-11	.187E-16	.179E-02	.289E-03	.228E-10	.2418E-18	.76E-04	.1457	36.1	6.28
.100E-11	.172E-16	.180E-02	.274E-03	.228E-10	.9844E-20	.63E-04	.1464	34.9	6.29
.100E-11	.158E-16	.180E-02	.261E-03	.228E-10	.3982E-21	.54E-04	.1466	33.7	6.31
.100E-11	.144E-16	.181E-02	.249E-03	.228E-10	.1605E-22	.47E-04	.1462	32.5	6.32
.100E-11	.130E-16	.181E-02	.239E-03	.228E-10	.6167E-24	.42E-04	.1455	31.3	6.34
.100E-11	.118E-16	.181E-02	.230E-03	.228E-10	.6069E-26	.42E-04	.1444	30.1	6.35

% NH3-N LOSS = .2977E+01, % UREA HYDROLYZED = 14.29

% N ACCOUNT= 100.0, % C ACCOUNT= 99.3, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.5

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
.56	16.6	16.8	25.0	27.6	27.5	-.4	.0	.01298	.00	.00	489.	285.

DAY	HOUR	MIN
187	0	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.151E-03	.192E-08	.240E-02	.733E-04	.570E-05	.7823E-01	.46E-01	.1969	18.8	6.92
.104E-03	.562E-09	.241E-02	.201E-03	.448E-05	.6424E-01	.67E-01	.1863	20.0	6.48
.785E-05	.310E-10	.241E-02	.316E-03	.810E-06	.5224E-01	.10E+00	.1478	21.2	6.29
.416E-07	.138E-12	.240E-02	.421E-03	.253E-07	.1408E-02	.40E-02	.0387	22.1	6.17
.654E-11	.237E-16	.239E-02	.428E-03	.798E-10	.8558E-06	.17E-03	.1195	23.0	6.17
.104E-11	.438E-17	.237E-02	.411E-03	.234E-10	.9425E-09	.15E-03	.1279	24.0	6.18
.100E-11	.485E-17	.236E-02	.392E-03	.229E-10	.1143E-11	.13E-03	.1342	24.8	6.21
.100E-11	.551E-17	.234E-02	.372E-03	.228E-10	.1535E-14	.11E-03	.1384	25.5	6.23
.100E-11	.617E-17	.233E-02	.354E-03	.228E-10	.2436E-17	.89E-04	.1413	26.1	6.25
.100E-11	.681E-17	.232E-02	.337E-03	.228E-10	.1643E-19	.75E-04	.1432	26.6	6.27
.100E-11	.740E-17	.230E-02	.323E-03	.228E-10	.7338E-21	.63E-04	.1443	26.9	6.29
.100E-11	.792E-17	.229E-02	.310E-03	.228E-10	.3848E-22	.54E-04	.1448	27.2	6.31
.100E-11	.836E-17	.228E-02	.299E-03	.228E-10	.1981E-23	.47E-04	.1448	27.4	6.32
.100E-11	.873E-17	.228E-02	.290E-03	.228E-10	.1002E-24	.42E-04	.1443	27.5	6.34
.100E-11	.901E-17	.228E-02	.283E-03	.228E-10	.2146E-26	.42E-04	.1432	27.6	6.35

% NH3-N LOSS = .3028E+01, % UREA HYDROLYZED = 17.97

% N ACCOUNT= 100.0, % C ACCOUNT= 100.6, % H ACCOUNT= 100.0, % CA ACCOUNT= 103.6

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
.28	14.1	14.6	21.2	24.1	26.1	2.9	.5	.01242	.00	.00	1156.	658.

DAY	HOUR	MIN
187	6	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.187E-03	.182E-08	.321E-02	.780E-04	.658E-05	.7685E-01	.43E-01	.1699	14.8	7.00
.140E-03	.461E-09	.321E-02	.256E-03	.543E-05	.6292E-01	.60E-01	.1650	15.6	6.49
.269E-04	.661E-10	.320E-02	.378E-03	.183E-05	.5226E-01	.94E-01	.1548	16.5	6.32
.539E-05	.109E-10	.319E-02	.508E-03	.632E-06	.1782E-01	.64E-01	.0884	17.3	6.19
.690E-08	.142E-13	.318E-02	.552E-03	.778E-08	.5995E-04	.43E-03	.1197	18.2	6.16
.342E-11	.807E-17	.316E-02	.529E-03	.514E-10	.2517E-06	.15E-03	.1280	18.9	6.18
.101E-11	.272E-17	.315E-02	.503E-03	.230E-10	.1021E-08	.12E-03	.1334	19.7	6.20
.100E-11	.308E-17	.314E-02	.478E-03	.228E-10	.3903E-11	.10E-03	.1372	20.4	6.22
.100E-11	.349E-17	.312E-02	.455E-03	.228E-10	.1400E-13	.87E-04	.1399	21.0	6.25
.100E-11	.392E-17	.311E-02	.434E-03	.228E-10	.4700E-16	.73E-04	.1417	21.6	6.27
.100E-11	.437E-17	.309E-02	.416E-03	.228E-10	.1478E-18	.62E-04	.1428	22.2	6.29
.100E-11	.482E-17	.308E-02	.400E-03	.228E-10	.4406E-21	.53E-04	.1433	22.7	6.30
.100E-11	.527E-17	.308E-02	.387E-03	.228E-10	.1501E-23	.47E-04	.1433	23.2	6.32
.100E-11	.571E-17	.307E-02	.377E-03	.228E-10	.1757E-25	.42E-04	.1427	23.7	6.33
.100E-11	.614E-17	.307E-02	.368E-03	.228E-10	.4673E-27	.42E-04	.1417	24.1	6.34

% NH3-N LOSS = .3037E+01, % UREA HYDROLYZED = 22.73
 % N ACCOUNT= 100.0, % C ACCOUNT= 100.9, % H ACCOUNT= 100.0, % CA ACCOUNT= 103.5

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
3.51	35.8	27.4	26.9	24.6	24.9	867.1	196.4	.01265	.00	.00	122.	67.

DAY	HOUR	MIN
187	12	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.256E-03	.209E-07	.379E-02	.103E-03	.808E-05	.4418E+00	.50E-01	.0260	33.4	7.04
.210E-03	.475E-08	.387E-02	.325E-03	.710E-05	.6161E-01	.60E-01	.1390	32.1	6.54
.683E-04	.931E-09	.391E-02	.471E-03	.338E-05	.4801E-01	.96E-01	.1396	30.9	6.38
.294E-04	.265E-09	.392E-02	.631E-03	.194E-05	.2123E-01	.96E-01	.1291	29.8	6.24
.383E-06	.255E-11	.392E-02	.763E-03	.110E-06	.6001E-03	.49E-02	.1249	28.8	6.16
.108E-09	.684E-15	.391E-02	.729E-03	.502E-09	.3078E-05	.17E-03	.1288	28.0	6.17
.113E-11	.699E-17	.391E-02	.684E-03	.248E-10	.1056E-07	.12E-03	.1334	27.3	6.20
.100E-11	.609E-17	.390E-02	.642E-03	.229E-10	.4682E-10	.10E-03	.1369	26.7	6.22
.100E-11	.607E-17	.389E-02	.604E-03	.228E-10	.2423E-12	.87E-04	.1394	26.1	6.24
.100E-11	.609E-17	.388E-02	.571E-03	.228E-10	.1295E-14	.73E-04	.1411	25.7	6.26
.100E-11	.614E-17	.388E-02	.542E-03	.228E-10	.6686E-17	.61E-04	.1421	25.4	6.28
.100E-11	.629E-17	.387E-02	.518E-03	.228E-10	.3244E-19	.53E-04	.1425	25.1	6.30
.100E-11	.629E-17	.386E-02	.498E-03	.228E-10	.1466E-21	.46E-04	.1424	24.9	6.32
.100E-11	.637E-17	.386E-02	.481E-03	.228E-10	.6285E-24	.41E-04	.1418	24.7	6.33
.100E-11	.646E-17	.386E-02	.467E-03	.228E-10	.2501E-26	.42E-04	.1408	24.6	6.34

% NH3-N LOSS = .3166E+01, % UREA HYDROLYZED = 31.28
 % N ACCOUNT= 100.0, % C ACCOUNT= 99.8, % H ACCOUNT= 100.0, % CA ACCOUNT= 102.7

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOOV	RAIN	RA	RH
4.04	35.2	29.7	33.0	29.2	26.0	467.1	107.1	.01313	.00	.00	105.	58.

DAY	HOUR	MIN
187	18	0

NH4AQ	NH3G	HC03	CO2G	NH4AD	UREA	CA	WA	TA	PH
.224E-03	.240E-07	.381E-02	.137E-03	.740E-05	.7276E+00	.32E-01	.0151	38.3	6.94
.442E-03	.325E-07	.394E-02	.207E-03	.116E-04	.1071E+00	.82E-01	.0514	38.3	6.78
.240E-03	.111E-07	.404E-02	.329E-03	.774E-05	.3056E-01	.95E-01	.1239	38.1	6.58
.141E-03	.414E-08	.409E-02	.506E-03	.546E-05	.1003E-01	.10E+00	.1302	37.7	6.40
.912E-05	.154E-09	.411E-02	.831E-03	.894E-06	.3895E-03	.25E-01	.1320	37.2	6.18
.443E-07	.674E-12	.412E-02	.858E-03	.266E-07	.1533E-04	.24E-02	.1335	36.6	6.17
.121E-09	.180E-14	.413E-02	.808E-03	.540E-09	.5064E-06	.23E-03	.1358	35.8	6.19
.159E-11	.232E-16	.413E-02	.758E-03	.311E-10	.1316E-07	.11E-03	.1382	35.1	6.21
.101E-11	.142E-16	.414E-02	.712E-03	.230E-10	.2741E-09	.88E-04	.1402	34.2	6.24
.100E-11	.136E-16	.415E-02	.671E-03	.228E-10	.4662E-11	.74E-04	.1416	33.4	6.26
.100E-11	.131E-16	.415E-02	.635E-03	.228E-10	.6573E-13	.62E-04	.1424	32.5	6.28
.100E-11	.125E-16	.416E-02	.604E-03	.228E-10	.7786E-15	.53E-04	.1427	31.7	6.30
.100E-11	.119E-16	.416E-02	.577E-03	.228E-10	.7856E-17	.46E-04	.1425	30.9	6.31
.100E-11	.113E-16	.416E-02	.553E-03	.228E-10	.6836E-19	.41E-04	.1418	30.0	6.33
.100E-11	.106E-16	.416E-02	.533E-03	.228E-10	.1649E-21	.42E-04	.1408	29.2	6.34

% NH3-N LOSS = .4225E+01, % UREA HYDROLYZED = 49.58

% N ACCOUNT= 99.9, % C ACCOUNT= 98.6, % H ACCOUNT= 100.0, % CA ACCOUNT= 101.6

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOOV	RAIN	RA	RH
.43	16.5	19.3	25.5	27.4	26.8	.0	.0	.01341	.00	.00	650.	378.

DAY	HOUR	MIN
188	0	0

NH4AQ	NH3G	HC03	CO2G	NH4AD	UREA	CA	WA	TA	PH
.226E-03	.381E-08	.433E-02	.121E-03	.744E-05	.5121E+00	.94E-01	.0241	20.4	6.96
.514E-03	.714E-08	.435E-02	.162E-03	.128E-04	.1005E+00	.10E+00	.0344	21.2	6.84
.342E-03	.356E-08	.435E-02	.241E-03	.979E-05	.1957E-01	.10E+00	.1228	22.0	6.67
.206E-03	.148E-08	.434E-02	.391E-03	.700E-05	.2900E-02	.98E-01	.1271	23.0	6.46
.108E-04	.443E-10	.433E-02	.754E-03	.100E-05	.4546E-04	.25E-01	.1302	23.8	6.18
.548E-07	.233E-12	.432E-02	.792E-03	.306E-07	.1024E-05	.27E-02	.1327	24.6	6.16
.170E-09	.819E-15	.431E-02	.755E-03	.676E-09	.3208E-07	.26E-03	.1350	25.2	6.19
.190E-11	.103E-16	.430E-02	.715E-03	.349E-10	.1013E-08	.11E-03	.1370	25.8	6.21
.101E-11	.610E-17	.429E-02	.679E-03	.230E-10	.2876E-10	.87E-04	.1387	26.2	6.23
.100E-11	.661E-17	.428E-02	.646E-03	.228E-10	.7285E-12	.73E-04	.1400	26.6	6.26
.100E-11	.715E-17	.427E-02	.617E-03	.228E-10	.1672E-13	.62E-04	.1409	26.9	6.28
.100E-11	.764E-17	.426E-02	.591E-03	.228E-10	.3545E-15	.53E-04	.1413	27.1	6.30
.100E-11	.807E-17	.426E-02	.570E-03	.228E-10	.7118E-17	.46E-04	.1412	27.3	6.31
.100E-11	.843E-17	.426E-02	.551E-03	.228E-10	.1394E-18	.41E-04	.1407	27.4	6.33
.100E-11	.873E-17	.425E-02	.536E-03	.228E-10	.1639E-20	.42E-04	.1397	27.4	6.34

% NH3-N LOSS = .4389E+01, % UREA HYDROLYZED = 56.59

% N ACCOUNT= 99.9, % C ACCOUNT= 98.7, % H ACCOUNT= 100.0, % CA ACCOUNT= 101.4

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
.78	14.7	17.9	22.1	24.5	25.8	3.0	.7	.01311	.00	.00	104173.	1000.

DAY	HOUR	MIN
188	6	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.242E-03	.302E-08	.502E-02	.125E-03	.779E-05	.4355E+00	.10E+00	.0297	17.0	7.00
.549E-03	.531E-08	.503E-02	.173E-03	.134E-04	.6221E-01	.10E+00	.0392	17.6	6.86
.394E-03	.280E-08	.501E-02	.256E-03	.107E-04	.1412E-01	.10E+00	.1224	18.2	6.69
.225E-03	.104E-08	.499E-02	.429E-03	.743E-05	.1000E-02	.94E-01	.1268	19.0	6.47
.110E-04	.280E-10	.497E-02	.845E-03	.101E-05	.2008E-04	.24E-01	.1300	19.7	6.17
.557E-07	.146E-12	.496E-02	.884E-03	.309E-07	.3840E-06	.28E-02	.1326	20.3	6.16
.173E-09	.514E-15	.494E-02	.840E-03	.684E-09	.8970E-08	.29E-03	.1348	20.9	6.18
.192E-11	.646E-17	.493E-02	.795E-03	.352E-10	.2492E-09	.11E-03	.1366	21.5	6.21
.101E-11	.382E-17	.492E-02	.753E-03	.231E-10	.7035E-11	.86E-04	.1380	22.0	6.23
.100E-11	.420E-17	.491E-02	.716E-03	.228E-10	.1853E-12	.72E-04	.1391	22.5	6.25
.100E-11	.464E-17	.490E-02	.684E-03	.228E-10	.4466E-14	.61E-04	.1398	23.0	6.27
.100E-11	.507E-17	.489E-02	.656E-03	.228E-10	.9890E-16	.52E-04	.1401	23.4	6.29
.100E-11	.550E-17	.488E-02	.633E-03	.228E-10	.2030E-17	.46E-04	.1400	23.8	6.31
.100E-11	.592E-17	.488E-02	.613E-03	.228E-10	.3927E-19	.41E-04	.1394	24.2	6.32
.100E-11	.633E-17	.487E-02	.597E-03	.228E-10	.6625E-21	.42E-04	.1384	24.5	6.34

% NH3-N LOSS = .4403E+01, % UREA HYDROLYZED = 59.76

% N ACCOUNT= 99.9, % C ACCOUNT= 99.0, % H ACCOUNT= 100.0, % CA ACCOUNT= 101.3

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
4.24	44.1	29.6	29.5	25.7	25.0	833.0	193.6	.01474	.00	.00	96.	53.

DAY	HOUR	MIN
188	12	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.245E-03	.477E-07	.427E-02	.144E-03	.784E-05	.9191E+00	.10E+00	.0142	43.1	7.00
.606E-03	.799E-07	.442E-02	.178E-03	.143E-04	.7865E-01	.95E-01	.0195	41.2	6.91
.487E-03	.365E-07	.457E-02	.255E-03	.124E-04	.6755E-02	.10E+00	.1151	39.0	6.75
.237E-03	.729E-08	.467E-02	.495E-03	.770E-05	.3349E-03	.94E-01	.1275	36.8	6.46
.112E-04	.143E-09	.472E-02	.964E-03	.102E-05	.1304E-04	.28E-01	.1316	34.8	6.17
.564E-07	.580E-12	.475E-02	.989E-03	.312E-07	.3597E-06	.37E-02	.1341	33.1	6.15
.174E-09	.162E-14	.479E-02	.924E-03	.687E-09	.7406E-08	.39E-03	.1359	31.6	6.17
.193E-11	.167E-16	.482E-02	.863E-03	.353E-10	.1361E-09	.12E-03	.1374	30.4	6.20
.101E-11	.830E-17	.484E-02	.809E-03	.231E-10	.2759E-11	.86E-04	.1385	29.3	6.23
.100E-11	.784E-17	.487E-02	.762E-03	.228E-10	.6388E-13	.72E-04	.1393	28.4	6.25
.100E-11	.759E-17	.489E-02	.722E-03	.228E-10	.1523E-14	.61E-04	.1397	27.6	6.27
.100E-11	.742E-17	.491E-02	.689E-03	.228E-10	.3479E-16	.52E-04	.1398	27.0	6.29
.100E-11	.730E-17	.492E-02	.660E-03	.228E-10	.7450E-18	.46E-04	.1395	26.4	6.31
.100E-11	.722E-17	.493E-02	.636E-03	.228E-10	.1495E-19	.40E-04	.1389	26.0	6.32
.100E-11	.717E-17	.494E-02	.615E-03	.228E-10	.2474E-21	.42E-04	.1378	25.7	6.34

% NH3-N LOSS = .4742E+01, % UREA HYDROLYZED = 64.04

% N ACCOUNT= 99.9, % C ACCOUNT= 98.5, % H ACCOUNT= 100.0, % CA ACCOUNT= 100.6

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
4.95	37.1	31.0	33.4	29.8	26.3	467.8	108.5	.01431	.00	.00	90.	49.

DAY	HOUR	MIN
188	18	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.214E-03	.235E-07	.272E-02	.111E-03	.717E-05	.9852E+00	.10E+00	.0146	39.7	6.89
.598E-03	.674E-07	.283E-02	.112E-03	.142E-04	.4456E-02	.92E-02	.0189	39.6	6.91
.564E-03	.499E-07	.295E-02	.146E-03	.136E-04	.6173E-05	.97E-01	.0584	39.4	6.81
.244E-03	.926E-08	.303E-02	.337E-03	.784E-05	.1330E-05	.89E-01	.1203	39.1	6.45
.115E-04	.210E-09	.308E-02	.669E-03	.104E-05	.2055E-06	.35E-01	.1300	38.5	6.16
.582E-07	.961E-12	.312E-02	.695E-03	.318E-07	.2283E-07	.74E-02	.1347	37.9	6.15
.178E-09	.289E-14	.315E-02	.657E-03	.698E-09	.1828E-08	.11E-02	.1373	37.1	6.17
.195E-11	.309E-16	.318E-02	.618E-03	.355E-10	.1076E-09	.19E-03	.1389	36.3	6.20
.101E-11	.156E-16	.321E-02	.581E-03	.231E-10	.4799E-11	.93E-04	.1399	35.4	6.22
.100E-11	.148E-16	.323E-02	.548E-03	.228E-10	.1678E-12	.74E-04	.1404	34.5	6.25
.100E-11	.141E-16	.326E-02	.519E-03	.228E-10	.4771E-14	.62E-04	.1406	33.5	6.27
.100E-11	.133E-16	.328E-02	.493E-03	.228E-10	.1151E-15	.53E-04	.1405	32.6	6.29
.100E-11	.126E-16	.329E-02	.471E-03	.228E-10	.2468E-17	.46E-04	.1401	31.6	6.31
.100E-11	.118E-16	.331E-02	.451E-03	.228E-10	.4929E-19	.41E-04	.1393	30.7	6.32
.100E-11	.110E-16	.331E-02	.433E-03	.228E-10	.2710E-21	.42E-04	.1383	29.8	6.33

% NH3-N LOSS = .6005E+01, % UREA HYDROLYZED = 66.19

% N ACCOUNT= 99.9, % C ACCOUNT= 98.2, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.7

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
2.57	19.6	23.3	27.0	28.1	27.2	.1	.0	.01465	.00	.00	109.	81.

DAY	HOUR	MIN
189	0	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.214E-03	.416E-08	.253E-02	.836E-04	.718E-05	.6526E+00	.10E+00	.0220	22.9	6.90
.600E-03	.126E-07	.260E-02	.858E-04	.142E-04	.2367E-03	.41E-01	.0246	23.6	6.90
.563E-03	.984E-08	.265E-02	.113E-03	.136E-04	.1513E-06	.94E-01	.0470	24.2	6.79
.245E-03	.202E-08	.268E-02	.261E-03	.785E-05	.2411E-07	.82E-01	.1205	24.8	6.44
.115E-04	.533E-10	.270E-02	.509E-03	.105E-05	.4603E-08	.33E-01	.1272	25.5	6.15
.586E-07	.279E-12	.271E-02	.531E-03	.320E-07	.5843E-09	.73E-02	.1317	26.1	6.14
.179E-09	.953E-15	.271E-02	.505E-03	.699E-09	.5446E-10	.11E-02	.1348	26.6	6.17
.195E-11	.116E-16	.272E-02	.479E-03	.355E-10	.3942E-11	.20E-03	.1368	27.0	6.19
.101E-11	.664E-17	.273E-02	.453E-03	.231E-10	.2304E-12	.95E-04	.1382	27.3	6.22
.100E-11	.714E-17	.273E-02	.430E-03	.228E-10	.1123E-13	.74E-04	.1390	27.6	6.24
.100E-11	.768E-17	.273E-02	.410E-03	.228E-10	.4708E-15	.62E-04	.1394	27.8	6.27
.100E-11	.817E-17	.274E-02	.393E-03	.228E-10	.1744E-16	.53E-04	.1395	28.0	6.29
.100E-11	.859E-17	.274E-02	.377E-03	.228E-10	.5859E-18	.46E-04	.1392	28.1	6.30
.100E-11	.895E-17	.274E-02	.364E-03	.228E-10	.1826E-19	.41E-04	.1386	28.1	6.32
.100E-11	.924E-17	.274E-02	.353E-03	.228E-10	.2705E-21	.42E-04	.1376	28.1	6.33

% NH3-N LOSS = .6203E+01, % UREA HYDROLYZED = 66.44

% N ACCOUNT= 99.9, % C ACCOUNT= 98.3, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.6

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
1.79	16.4	19.4	23.7	25.7	26.3	2.8	.7	.01412	.00	.00	162.	121.

DAY	HOUR	MIN
189	6	0

NH4AQ	NH3G	HC03	CO2G	NH4AD	UREA	CA	WA	TA	PH
.227E-03	.320E-08	.261E-02	.750E-04	.747E-05	.5300E+00	.10E+00	.0268	19.1	6.94
.600E-03	.795E-08	.266E-02	.865E-04	.142E-04	.1450E-03	.64E-01	.0282	19.7	6.89
.563E-03	.610E-08	.269E-02	.114E-03	.136E-04	.7088E-07	.91E-01	.0503	20.2	6.78
.245E-03	.124E-08	.270E-02	.262E-03	.785E-05	.3067E-08	.77E-01	.1205	20.7	6.42
.116E-04	.335E-10	.271E-02	.498E-03	.105E-05	.5656E-09	.31E-01	.1266	21.4	6.15
.588E-07	.176E-12	.271E-02	.517E-03	.320E-07	.7293E-10	.71E-02	.1308	22.0	6.13
.179E-09	.607E-15	.271E-02	.490E-03	.699E-09	.6884E-11	.11E-02	.1337	22.5	6.16
.195E-11	.747E-17	.272E-02	.463E-03	.355E-10	.5054E-12	.21E-03	.1358	23.1	6.19
.101E-11	.435E-17	.272E-02	.438E-03	.231E-10	.3006E-13	.94E-04	.1372	23.5	6.21
.100E-11	.477E-17	.272E-02	.415E-03	.228E-10	.1496E-14	.73E-04	.1380	24.0	6.24
.100E-11	.525E-17	.272E-02	.396E-03	.228E-10	.6400E-16	.61E-04	.1385	24.4	6.26
.100E-11	.573E-17	.272E-02	.379E-03	.228E-10	.2410E-17	.53E-04	.1385	24.7	6.28
.100E-11	.620E-17	.272E-02	.364E-03	.228E-10	.8157E-19	.46E-04	.1382	25.1	6.30
.100E-11	.665E-17	.272E-02	.352E-03	.228E-10	.2528E-20	.41E-04	.1376	25.4	6.32
.100E-11	.707E-17	.272E-02	.342E-03	.228E-10	.5840E-22	.41E-04	.1366	25.7	6.33

% NH3-N LOSS = .6256E+01, % UREA HYDROLYZED = 66.89

% N ACCOUNT= 99.9, % C ACCOUNT= 98.5, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.7

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
4.03	45.2	29.8	29.8	26.3	25.6	872.9	205.6	.01473	.00	.00	99.	55.

DAY	HOUR	MIN
189	12	0

NH4AQ	NH3G	HC03	CO2G	NH4AD	UREA	CA	WA	TA	PH
.228E-03	.395E-07	.224E-02	.902E-04	.749E-05	.9951E+00	.10E+00	.0141	43.6	6.92
.599E-03	.780E-07	.232E-02	.993E-04	.142E-04	.1104E-03	.50E-01	.0188	41.6	6.88
.562E-03	.467E-07	.238E-02	.131E-03	.136E-04	.2318E-07	.84E-01	.0432	39.8	6.77
.245E-03	.736E-08	.243E-02	.297E-03	.786E-05	.5226E-09	.75E-01	.1176	37.8	6.41
.116E-04	.154E-09	.246E-02	.541E-03	.105E-05	.4707E-10	.32E-01	.1271	35.8	6.14
.591E-07	.638E-12	.249E-02	.549E-03	.321E-07	.6979E-11	.79E-02	.1316	34.1	6.13
.179E-09	.176E-14	.251E-02	.512E-03	.700E-09	.7995E-12	.13E-02	.1343	32.6	6.16
.195E-11	.179E-16	.253E-02	.476E-03	.355E-10	.6796E-13	.23E-03	.1362	31.3	6.18
.101E-11	.878E-17	.255E-02	.445E-03	.231E-10	.4506E-14	.97E-04	.1374	30.1	6.21
.100E-11	.831E-17	.256E-02	.418E-03	.228E-10	.2433E-15	.73E-04	.1381	29.2	6.24
.100E-11	.805E-17	.258E-02	.395E-03	.228E-10	.1108E-16	.61E-04	.1383	28.4	6.26
.100E-11	.787E-17	.259E-02	.375E-03	.228E-10	.4377E-18	.52E-04	.1383	27.7	6.28
.100E-11	.774E-17	.260E-02	.358E-03	.228E-10	.1535E-19	.46E-04	.1379	27.2	6.30
.100E-11	.765E-17	.261E-02	.344E-03	.228E-10	.4873E-21	.40E-04	.1371	26.7	6.32
.100E-11	.758E-17	.261E-02	.332E-03	.228E-10	.1184E-22	.41E-04	.1361	26.3	6.33

% NH3-N LOSS = .6579E+01, % UREA HYDROLYZED = 67.20

% N ACCOUNT= 99.9, % C ACCOUNT= 98.3, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.3

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOOV	RAIN	RA	RH
4.49	36.9	31.4	33.5	30.1	26.7	460.9	109.1	.01360	.00	.00	96.	53.

DAY	HOUR	MIN
189	18	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.203E-03	.207E-07	.149E-02	.741E-04	.693E-05	.9913E+00	.10E+00	.0141	40.7	6.81
.587E-03	.687E-07	.155E-02	.663E-04	.140E-04	.1284E-03	.34E-01	.0164	40.6	6.98
.559E-03	.488E-07	.160E-02	.895E-04	.135E-04	.1007E-07	.28E-01	.0202	40.4	6.76
.247E-03	.901E-08	.163E-02	.209E-03	.790E-05	.8319E-11	.67E-01	.0875	40.0	6.40
.118E-04	.223E-09	.165E-02	.385E-03	.106E-05	.1547E-12	.35E-01	.1226	39.4	6.14
.603E-07	.103E-11	.167E-02	.395E-03	.326E-07	.3331E-13	.11E-01	.1310	38.7	6.12
.180E-09	.303E-14	.168E-02	.371E-03	.702E-09	.7373E-14	.24E-02	.1351	38.0	6.15
.195E-11	.322E-16	.170E-02	.347E-03	.355E-10	.1290E-14	.44E-03	.1373	37.1	6.18
.101E-11	.162E-16	.171E-02	.324E-03	.231E-10	.1706E-15	.13E-03	.1396	36.2	6.21
.100E-11	.154E-16	.173E-02	.304E-03	.228E-10	.1727E-16	.78E-04	.1392	35.2	6.23
.100E-11	.146E-16	.174E-02	.287E-03	.228E-10	.1375E-17	.63E-04	.1394	34.2	6.26
.100E-11	.138E-16	.175E-02	.271E-03	.228E-10	.8866E-19	.54E-04	.1392	33.2	6.28
.100E-11	.130E-16	.175E-02	.257E-03	.228E-10	.4758E-20	.47E-04	.1396	32.1	6.30
.100E-11	.121E-16	.176E-02	.245E-03	.228E-10	.2175E-21	.41E-04	.1379	31.1	6.31
.100E-11	.112E-16	.176E-02	.235E-03	.228E-10	.2594E-23	.41E-04	.1368	30.1	6.33

% NH3-N LOSS = .7701E+01, % UREA HYDROLYZED = 67.32

% N ACCOUNT= 99.8, % C ACCOUNT= 98.2, % H ACCOUNT= 100.0, % CA ACCOUNT= 98.7

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOOV	RAIN	RA	RH
2.47	17.7	22.6	25.1	27.0	27.2	.1	.0	.01459	.00	.00	146.	113.

DAY	HOUR	MIN
190	0	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.239E-03	.321E-08	.188E-02	.629E-04	.772E-05	.3120E-01	.49E-01	.1929	20.0	6.88
.637E-03	.870E-08	.196E-02	.716E-04	.148E-04	.2371E-01	.70E-01	.1836	20.9	6.85
.595E-03	.760E-08	.196E-02	.857E-04	.141E-04	.1725E-01	.10E+00	.1326	21.7	6.78
.248E-03	.143E-08	.197E-02	.210E-03	.791E-05	.2490E-03	.61E-01	.0902	22.6	6.39
.119E-04	.412E-10	.196E-02	.383E-03	.107E-05	.1856E-06	.32E-01	.1187	23.4	6.13
.606E-07	.222E-12	.196E-02	.394E-03	.327E-07	.2262E-09	.11E-01	.1272	24.1	6.12
.180E-09	.751E-15	.195E-02	.371E-03	.702E-09	.3690E-12	.24E-02	.1318	24.7	6.15
.195E-11	.924E-17	.194E-02	.348E-03	.355E-10	.7171E-15	.47E-03	.1346	25.2	6.18
.101E-11	.538E-17	.193E-02	.327E-03	.231E-10	.6567E-17	.13E-03	.1364	25.7	6.20
.100E-11	.587E-17	.192E-02	.308E-03	.228E-10	.6339E-18	.78E-04	.1374	26.1	6.23
.100E-11	.642E-17	.192E-02	.291E-03	.228E-10	.6163E-19	.63E-04	.1379	26.4	6.25
.100E-11	.693E-17	.191E-02	.276E-03	.228E-10	.5062E-20	.53E-04	.1379	26.7	6.28
.100E-11	.739E-17	.190E-02	.264E-03	.228E-10	.3590E-21	.47E-04	.1377	26.8	6.29
.100E-11	.778E-17	.190E-02	.254E-03	.228E-10	.2234E-22	.41E-04	.1370	27.0	6.31
.100E-11	.809E-17	.190E-02	.245E-03	.228E-10	.5152E-24	.41E-04	.1360	27.0	6.33

% NH3-N LOSS = .7851E+01, % UREA HYDROLYZED = 70.42

% N ACCOUNT= 100.1, % C ACCOUNT= 99.3, % H ACCOUNT= 100.0, % CA ACCOUNT= 102.4

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
.64	14.7	17.4	21.7	24.0	25.8	2.6	.4	.01275	.00	.00	126961.	1000.

DAY	HOUR	MIN
190	6	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.283E-03	.281E-08	.280E-02	.812E-04	.864E-05	.2985E-01	.47E-01	.1613	16.4	6.93
.699E-03	.585E-08	.279E-02	.105E-03	.157E-04	.2136E-01	.61E-01	.1560	17.1	6.82
.657E-03	.549E-08	.275E-02	.114E-03	.151E-04	.1533E-01	.96E-01	.1464	17.9	6.78
.268E-03	.100E-08	.272E-02	.274E-03	.834E-05	.2796E-02	.91E-01	.1304	18.6	6.40
.120E-04	.259E-10	.270E-02	.513E-03	.107E-05	.2493E-04	.31E-01	.1231	19.3	6.12
.608E-07	.139E-12	.268E-02	.525E-03	.328E-07	.8584E-07	.10E-01	.1265	19.9	6.11
.180E-09	.470E-15	.267E-02	.493E-03	.703E-09	.3139E-09	.24E-02	.1305	20.6	6.14
.195E-11	.581E-17	.265E-02	.461E-03	.355E-10	.1120E-11	.47E-03	.1334	21.1	6.17
.101E-11	.341E-17	.264E-02	.432E-03	.231E-10	.3739E-14	.13E-03	.1352	21.7	6.20
.100E-11	.378E-17	.263E-02	.406E-03	.228E-10	.1162E-16	.78E-04	.1363	22.1	6.23
.100E-11	.420E-17	.262E-02	.384E-03	.228E-10	.4070E-19	.62E-04	.1369	22.6	6.25
.100E-11	.462E-17	.261E-02	.365E-03	.228E-10	.7084E-21	.53E-04	.1370	23.0	6.27
.100E-11	.505E-17	.260E-02	.349E-03	.228E-10	.4320E-22	.46E-04	.1367	23.4	6.29
.100E-11	.545E-17	.259E-02	.336E-03	.228E-10	.2609E-23	.41E-04	.1361	23.7	6.31
.100E-11	.584E-17	.259E-02	.325E-03	.228E-10	.8905E-25	.41E-04	.1351	24.0	6.32

% NH3-N LOSS = .7875E+01, % UREA HYDROLYZED = 74.91

% N ACCOUNT= 100.1, % C ACCOUNT= 99.4, % H ACCOUNT= 100.0, % CA ACCOUNT= 102.4

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
3.25	37.5	29.7	27.2	24.4	24.8	874.1	207.2	.01399	.00	.00	122.	67.

DAY	HOUR	MIN
190	12	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.349E-03	.392E-07	.291E-02	.111E-03	.992E-05	.2436E+00	.53E-01	.0157	39.2	6.92
.803E-03	.546E-07	.303E-02	.132E-03	.172E-04	.1704E-01	.63E-01	.1360	36.0	6.84
.747E-03	.355E-07	.314E-02	.143E-03	.164E-04	.1039E-01	.94E-01	.1410	33.2	6.81
.302E-03	.465E-08	.318E-02	.353E-03	.902E-05	.1709E-02	.99E-01	.1381	31.2	6.41
.127E-04	.847E-10	.319E-02	.683E-03	.111E-05	.1063E-03	.39E-01	.1332	29.7	6.12
.624E-07	.358E-12	.319E-02	.691E-03	.333E-07	.2547E-05	.11E-01	.1309	28.5	6.11
.181E-09	.100E-14	.320E-02	.642E-03	.705E-09	.2136E-07	.24E-02	.1317	27.5	6.14
.196E-11	.107E-16	.320E-02	.596E-03	.356E-10	.8398E-10	.48E-03	.1334	26.8	6.17
.101E-11	.557E-17	.320E-02	.554E-03	.231E-10	.2398E-12	.13E-03	.1349	26.2	6.20
.100E-11	.554E-17	.321E-02	.488E-03	.228E-10	.7042E-15	.78E-04	.1359	25.7	6.22
.100E-11	.563E-17	.321E-02	.462E-03	.228E-10	.2391E-17	.62E-04	.1365	25.3	6.25
.100E-11	.573E-17	.321E-02	.440E-03	.228E-10	.8967E-20	.53E-04	.1365	25.0	6.27
.100E-11	.585E-17	.321E-02	.421E-03	.228E-10	.4027E-22	.46E-04	.1362	24.8	6.29
.100E-11	.595E-17	.321E-02	.406E-03	.228E-10	.5292E-24	.40E-04	.1356	24.6	6.31
.100E-11	.604E-17	.321E-02	.384E-03	.228E-10	.1689E-25	.41E-04	.1346	24.4	6.32

% NH3-N LOSS = .8054E+01, % UREA HYDROLYZED = 81.73

% N ACCOUNT= 100.0, % C ACCOUNT= 98.7, % H ACCOUNT= 100.0, % CA ACCOUNT= 101.4

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
4.79	36.8	32.0	33.4	29.5	25.9	458.4	110.2	.01364	.00	.00	94.	51.

DAY	HOUR	MIN
190	18	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.313E-03	.263E-07	.219E-02	.113E-03	.923E-05	.2397E+00	.34E-01	.0150	39.4	6.79
.106E-02	.160E-06	.230E-02	.664E-04	.207E-04	.2730E-02	.79E-01	.0381	39.3	7.04
.919E-03	.101E-06	.248E-02	.950E-04	.188E-04	.2892E-03	.93E-01	.1270	39.1	6.92
.336E-03	.116E-07	.257E-02	.302E-03	.969E-05	.2992E-04	.97E-01	.1343	38.7	6.43
.140E-04	.223E-09	.261E-02	.625E-03	.119E-05	.4278E-05	.52E-01	.1363	38.2	6.12
.726E-07	.105E-11	.264E-02	.643E-03	.368E-07	.4950E-06	.18E-01	.1362	37.5	6.10
.223E-09	.319E-14	.266E-02	.601E-03	.809E-09	.3920E-07	.43E-02	.1359	36.7	6.13
.217E-11	.306E-16	.268E-02	.560E-03	.381E-10	.2075E-08	.84E-03	.1361	35.9	6.16
.102E-11	.140E-16	.270E-02	.522E-03	.231E-10	.7690E-10	.19E-03	.1367	35.0	6.19
.100E-11	.133E-16	.272E-02	.488E-03	.228E-10	.2115E-11	.85E-04	.1372	34.1	6.22
.100E-11	.128E-16	.274E-02	.458E-03	.228E-10	.4511E-13	.64E-04	.1374	33.2	6.24
.100E-11	.123E-16	.275E-02	.432E-03	.228E-10	.7674E-15	.54E-04	.1373	32.2	6.27
.100E-11	.117E-16	.276E-02	.409E-03	.228E-10	.1063E-16	.47E-04	.1369	31.3	6.29
.100E-11	.111E-16	.277E-02	.390E-03	.228E-10	.1215E-18	.41E-04	.1361	30.4	6.31
.100E-11	.105E-16	.277E-02	.373E-03	.228E-10	.3177E-21	.41E-04	.1351	29.5	6.32

% NH3-N LOSS = .9377E+01, % UREA HYDROLYZED = 91.31

% N ACCOUNT= 99.9, % C ACCOUNT= 98.4, % H ACCOUNT= 100.0, % CA ACCOUNT= 100.4

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
1.59	18.1	22.5	26.3	27.8	26.9	.1	.0	.01436	.00	.00	173.	128.

DAY	HOUR	MIN
191	0	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.316E-03	.445E-08	.232E-02	.989E-04	.930E-05	.1563E+00	.10E+00	.0225	22.4	6.79
.107E-02	.291E-07	.235E-02	.564E-04	.208E-04	.5111E-04	.79E-01	.0268	23.1	7.04
.922E-03	.186E-07	.239E-02	.848E-04	.188E-04	.8396E-05	.90E-01	.1240	23.8	6.87
.337E-03	.256E-08	.241E-02	.249E-03	.971E-05	.9163E-06	.92E-01	.1295	24.6	6.41
.141E-04	.576E-10	.242E-02	.504E-03	.120E-05	.1251E-06	.50E-01	.1325	25.3	6.11
.735E-07	.312E-12	.242E-02	.520E-03	.371E-07	.1490E-07	.18E-01	.1340	25.9	6.10
.227E-09	.109E-14	.242E-02	.489E-03	.819E-09	.1330E-08	.45E-02	.1347	26.4	6.13
.222E-11	.120E-16	.242E-02	.458E-03	.387E-10	.8736E-10	.92E-03	.1353	26.8	6.16
.102E-11	.611E-17	.242E-02	.430E-03	.231E-10	.4395E-11	.21E-03	.1357	27.2	6.19
.100E-11	.658E-17	.242E-02	.405E-03	.228E-10	.1786E-12	.88E-04	.1361	27.4	6.22
.100E-11	.712E-17	.242E-02	.382E-03	.228E-10	.6141E-14	.64E-04	.1364	27.6	6.24
.100E-11	.761E-17	.242E-02	.363E-03	.228E-10	.1849E-15	.54E-04	.1364	27.8	6.27
.100E-11	.804E-17	.242E-02	.346E-03	.228E-10	.5013E-17	.47E-04	.1361	27.8	6.29
.100E-11	.838E-17	.242E-02	.332E-03	.228E-10	.1247E-18	.41E-04	.1354	27.8	6.30
.100E-11	.864E-17	.242E-02	.319E-03	.228E-10	.1479E-20	.41E-04	.1345	27.8	6.32

% NH3-N LOSS = .9571E+01, % UREA HYDROLYZED = 91.78

% N ACCOUNT= 99.8, % C ACCOUNT= 98.5, % H ACCOUNT= 100.0, % CA ACCOUNT= 100.2

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOOV	RAIN	RA	RH
.64	14.9	17.8	22.8	24.9	26.0	2.7	.7	.01344	.00	.00	553.	427.

DAY	HOURL	MIN
191	6	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.334E-03	.288E-08	.287E-02	.111E-03	.963E-05	.1215E+00	.10E+00	.0275	17.6	6.81
.107E-02	.162E-07	.288E-02	.683E-04	.208E-04	.3426E-04	.81E-01	.0326	18.2	7.02
.921E-03	.951E-08	.287E-02	.109E-03	.188E-04	.1418E-05	.89E-01	.1238	18.9	6.82
.337E-03	.142E-08	.286E-02	.292E-03	.971E-05	.1533E-06	.88E-01	.1282	19.6	6.40
.142E-04	.329E-10	.285E-02	.574E-03	.120E-05	.1953E-07	.48E-01	.1311	20.3	6.10
.737E-07	.180E-12	.285E-02	.589E-03	.372E-07	.2202E-08	.17E-01	.1329	21.0	6.09
.228E-09	.638E-15	.284E-02	.552E-03	.820E-09	.1909E-09	.45E-02	.1340	21.6	6.12
.222E-11	.713E-17	.283E-02	.516E-03	.387E-10	.1252E-10	.93E-03	.1348	22.1	6.16
.102E-11	.371E-17	.283E-02	.483E-03	.231E-10	.6428E-12	.21E-03	.1352	22.7	6.19
.100E-11	.409E-17	.282E-02	.454E-03	.228E-10	.2696E-13	.88E-04	.1355	23.1	6.21
.100E-11	.455E-17	.282E-02	.429E-03	.228E-10	.9594E-15	.64E-04	.1357	23.5	6.24
.100E-11	.501E-17	.281E-02	.407E-03	.228E-10	.2984E-16	.53E-04	.1356	23.9	6.26
.100E-11	.547E-17	.281E-02	.389E-03	.228E-10	.8299E-18	.46E-04	.1352	24.3	6.28
.100E-11	.592E-17	.280E-02	.373E-03	.228E-10	.2098E-19	.41E-04	.1345	24.6	6.30
.100E-11	.635E-17	.280E-02	.360E-03	.228E-10	.4071E-21	.41E-04	.1336	24.9	6.32

% NH3-N LOSS = .9586E+01, % UREA HYDROLYZED = 92.21

% N ACCOUNT= 99.8, % C ACCOUNT= 98.7, % H ACCOUNT= 100.0, % CA ACCOUNT= 100.2

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOOV	RAIN	RA	RH
4.21	46.0	31.9	30.1	26.0	25.2	967.3	211.4	.01495	.00	.00	97.	53.

DAY	HOURL	MIN
191	12	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.337E-03	.497E-07	.209E-02	.116E-03	.969E-05	.2310E+00	.10E+00	.0139	45.1	6.79
.106E-02	.211E-06	.218E-02	.712E-04	.207E-04	.3157E-04	.62E-01	.0178	42.9	7.01
.921E-03	.860E-07	.231E-02	.124E-03	.188E-04	.1174E-06	.83E-01	.1124	40.6	6.78
.338E-03	.988E-08	.239E-02	.312E-03	.972E-05	.1480E-07	.87E-01	.1294	38.2	6.38
.143E-04	.175E-09	.243E-02	.593E-03	.120E-05	.2200E-08	.50E-01	.1323	36.1	6.10
.742E-07	.742E-12	.246E-02	.596E-03	.373E-07	.2877E-09	.19E-01	.1341	34.2	6.09
.228E-09	.207E-14	.249E-02	.551E-03	.821E-09	.2918E-10	.51E-02	.1351	32.6	6.12
.222E-11	.188E-16	.251E-02	.510E-03	.387E-10	.2207E-11	.11E-02	.1356	31.2	6.15
.102E-11	.814E-17	.254E-02	.473E-03	.231E-10	.1267E-12	.23E-03	.1359	30.0	6.18
.100E-11	.766E-17	.256E-02	.442E-03	.228E-10	.5749E-14	.91E-04	.1360	29.0	6.21
.100E-11	.743E-17	.258E-02	.415E-03	.228E-10	.2155E-15	.64E-04	.1359	28.1	6.24
.100E-11	.729E-17	.259E-02	.392E-03	.228E-10	.6939E-17	.53E-04	.1356	27.4	6.26
.100E-11	.719E-17	.261E-02	.372E-03	.228E-10	.1979E-18	.46E-04	.1350	26.9	6.28
.100E-11	.714E-17	.261E-02	.356E-03	.228E-10	.5098E-20	.41E-04	.1343	26.4	6.30
.100E-11	.711E-17	.262E-02	.342E-03	.228E-10	.1008E-21	.41E-04	.1333	26.0	6.32

% NH3-N LOSS = .9937E+01, % UREA HYDROLYZED = 92.51

% N ACCOUNT= 99.8, % C ACCOUNT= 98.5, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.7

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
4.89	38.1	33.3	33.9	30.3	26.6	441.6	107.9	.01515	.00	.00	92.	50.

DAY	HOURL	MIN
191	18	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.309E-03	.237E-07	.114E-02	.796E-04	.916E-05	.2172E+00	.97E-01	.0145	41.2	6.67
.103E-02	.168E-06	.120E-02	.387E-04	.202E-04	.2273E-04	.83E-03	.0189	41.1	7.00
.918E-03	.942E-07	.127E-02	.712E-04	.188E-04	.4320E-08	.73E-01	.0461	40.8	6.76
.342E-03	.122E-07	.132E-02	.182E-03	.979E-05	.2907E-10	.80E-01	.1201	40.4	6.37
.146E-04	.259E-09	.134E-02	.347E-03	.122E-05	.5158E-11	.53E-01	.1300	39.9	6.09
.758E-07	.124E-11	.136E-02	.354E-03	.379E-07	.1468E-11	.24E-01	.1345	39.1	6.09
.229E-09	.369E-14	.138E-02	.331E-03	.823E-09	.3281E-12	.76E-02	.1366	38.3	6.12
.223E-11	.353E-16	.139E-02	.307E-03	.387E-10	.5393E-13	.18E-02	.1375	37.4	6.15
.102E-11	.157E-16	.141E-02	.286E-03	.231E-10	.6539E-14	.39E-03	.1377	36.5	6.18
.100E-11	.149E-16	.142E-02	.267E-03	.228E-10	.5965E-15	.12E-03	.1376	35.5	6.21
.100E-11	.143E-16	.143E-02	.250E-03	.228E-10	.4200E-16	.69E-04	.1373	34.4	6.23
.100E-11	.136E-16	.144E-02	.235E-03	.228E-10	.2345E-17	.55E-04	.1368	33.4	6.26
.100E-11	.128E-16	.145E-02	.222E-03	.228E-10	.1068E-18	.47E-04	.1361	32.3	6.28
.100E-11	.120E-16	.146E-02	.211E-03	.228E-10	.4063E-20	.41E-04	.1352	31.3	6.30
.100E-11	.112E-16	.146E-02	.201E-03	.228E-10	.3563E-22	.41E-04	.1342	30.3	6.32

% NH3-N LOSS = .1129E+02, % UREA HYDROLYZED = 92.63

% N ACCOUNT= 99.7, % C ACCOUNT= 98.4, % H ACCOUNT= 100.0, % CA ACCOUNT= 98.9

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
2.89	21.0	23.4	27.7	28.7	27.5	.1	.0	.01372	.00	.00	182.	96.

DAY	HOURL	MIN
192	0	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.311E-03	.371E-08	.109E-02	.642E-04	.918E-05	.1520E+00	.10E+00	.0205	23.7	6.65
.102E-02	.292E-07	.113E-02	.304E-04	.201E-04	.2346E-04	.27E-01	.0233	24.4	7.00
.917E-03	.162E-07	.117E-02	.551E-04	.188E-04	.4113E-08	.75E-01	.0338	25.1	6.75
.343E-03	.262E-08	.119E-02	.141E-03	.980E-05	.1096E-10	.76E-01	.1204	25.8	6.36
.146E-04	.648E-10	.120E-02	.267E-03	.122E-05	.1377E-12	.51E-01	.1268	26.5	6.09
.763E-07	.354E-12	.120E-02	.274E-03	.381E-07	.2584E-13	.23E-01	.1310	27.1	6.08
.229E-09	.120E-14	.121E-02	.258E-03	.824E-09	.6125E-14	.77E-02	.1337	27.5	6.11
.223E-11	.131E-16	.122E-02	.241E-03	.387E-10	.1117E-14	.19E-02	.1352	27.9	6.14
.102E-11	.663E-17	.122E-02	.227E-03	.231E-10	.1577E-15	.43E-03	.1360	28.2	6.18
.100E-11	.713E-17	.123E-02	.213E-03	.228E-10	.1760E-16	.13E-03	.1363	28.5	6.20
.100E-11	.772E-17	.123E-02	.201E-03	.228E-10	.1595E-17	.71E-04	.1363	28.6	6.23
.100E-11	.827E-17	.123E-02	.191E-03	.228E-10	.1201E-18	.55E-04	.1360	28.7	6.26
.100E-11	.874E-17	.124E-02	.182E-03	.228E-10	.7672E-20	.47E-04	.1355	28.8	6.28
.100E-11	.914E-17	.124E-02	.174E-03	.228E-10	.4221E-21	.42E-04	.1348	28.8	6.30
.100E-11	.944E-17	.124E-02	.168E-03	.228E-10	.8218E-23	.41E-04	.1338	28.7	6.31

% NH3-N LOSS = .1150E+02, % UREA HYDROLYZED = 92.73

% N ACCOUNT= 99.7, % C ACCOUNT= 98.4, % H ACCOUNT= 100.0, % CA ACCOUNT= 98.9

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOCV	RAIN	RA	RH
1.07	17.4	20.4	24.9	26.4	26.7	2.4	.6	.01497	.00	.00	449.	241.

DAY	HOUR	MIN
192	6	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.324E-03	.283E-08	.127E-02	.698E-04	.944E-05	.1174E+00	.10E+00	.0252	20.5	6.67
.102E-02	.196E-07	.128E-02	.342E-04	.201E-04	.2704E-04	.45E-01	.0263	21.1	6.98
.916E-03	.108E-07	.129E-02	.599E-04	.188E-04	.6466E-08	.76E-01	.0358	21.6	6.75
.343E-03	.171E-08	.129E-02	.152E-03	.981E-05	.2112E-10	.74E-01	.1207	22.2	6.34
.147E-04	.427E-10	.128E-02	.279E-03	.123E-05	.1388E-12	.49E-01	.1261	22.8	6.08
.766E-07	.234E-12	.128E-02	.283E-03	.381E-07	.3208E-14	.22E-01	.1299	23.3	6.08
.230E-09	.795E-15	.128E-02	.264E-03	.825E-09	.5551E-15	.75E-02	.1324	23.8	6.11
.223E-11	.874E-17	.128E-02	.246E-03	.387E-10	.9706E-16	.19E-02	.1341	24.3	6.14
.102E-11	.450E-17	.127E-02	.229E-03	.231E-10	.1328E-16	.44E-03	.1350	24.7	6.17
.100E-11	.492E-17	.127E-02	.214E-03	.228E-10	.1447E-17	.13E-03	.1355	25.1	6.20
.100E-11	.544E-17	.127E-02	.202E-03	.228E-10	.1296E-18	.71E-04	.1356	25.4	6.23
.100E-11	.595E-17	.126E-02	.191E-03	.228E-10	.9545E-20	.55E-04	.1353	25.7	6.25
.100E-11	.645E-17	.126E-02	.181E-03	.228E-10	.6035E-21	.47E-04	.1348	26.0	6.28
.100E-11	.692E-17	.126E-02	.173E-03	.228E-10	.3296E-22	.41E-04	.1341	26.2	6.30
.100E-11	.737E-17	.126E-02	.167E-03	.228E-10	.1023E-23	.41E-04	.1331	26.4	6.31

% NH3-N LOSS = .1156E+02, % UREA HYDROLYZED = 93.11

% N ACCOUNT= 99.7, % C ACCOUNT= 98.5, % H ACCOUNT= 100.0, % CA ACCOUNT= 98.9

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOCV	RAIN	RA	RH
3.68	48.1	33.6	30.8	27.2	26.2	846.2	208.5	.01536	.00	.00	107.	59.

DAY	HOUR	MIN
192	12	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.329E-03	.407E-07	.108E-02	.842E-04	.955E-05	.2052E+00	.10E+00	.0138	46.6	6.65
.101E-02	.212E-06	.112E-02	.405E-04	.200E-04	.2611E-04	.30E-01	.0177	44.3	6.97
.915E-03	.911E-07	.117E-02	.712E-04	.188E-04	.2182E-08	.70E-01	.0265	42.3	6.74
.344E-03	.109E-07	.120E-02	.180E-03	.983E-05	.2763E-10	.70E-01	.1164	40.1	6.33
.148E-04	.209E-09	.122E-02	.320E-03	.123E-05	.8568E-12	.49E-01	.1268	37.9	6.08
.771E-07	.888E-12	.124E-02	.319E-03	.383E-07	.1775E-13	.23E-01	.1309	36.0	6.07
.230E-09	.240E-14	.125E-02	.294E-03	.825E-09	.2801E-15	.80E-02	.1332	34.3	6.10
.223E-11	.216E-16	.126E-02	.270E-03	.387E-10	.1033E-16	.21E-02	.1346	32.9	6.14
.102E-11	.935E-17	.127E-02	.250E-03	.231E-10	.1229E-17	.48E-03	.1353	31.6	6.17
.100E-11	.879E-17	.129E-02	.232E-03	.228E-10	.1416E-18	.14E-03	.1357	30.6	6.20
.100E-11	.851E-17	.129E-02	.217E-03	.228E-10	.1320E-19	.72E-04	.1356	29.7	6.23
.100E-11	.832E-17	.130E-02	.204E-03	.228E-10	.1012E-20	.55E-04	.1353	28.9	6.25
.100E-11	.818E-17	.131E-02	.193E-03	.228E-10	.6540E-22	.47E-04	.1347	28.2	6.27
.100E-11	.807E-17	.131E-02	.184E-03	.228E-10	.3625E-23	.41E-04	.1339	27.7	6.29
.100E-11	.798E-17	.131E-02	.176E-03	.228E-10	.1270E-24	.41E-04	.1329	27.2	6.31

% NH3-N LOSS = .1183E+02, % UREA HYDROLYZED = 93.40

% N ACCOUNT= 99.7, % C ACCOUNT= 98.4, % H ACCOUNT= 100.0, % CA ACCOUNT= 98.5

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
2.71	41.1	33.5	35.5	31.4	27.4	432.8	108.6	.01757	.00	.00	137.	76.

DAY	HOURL	MIN
192	18	0

NH4AQ	NH3G	HC03	CO2G	NH4AD	UREA	CA	WA	TA	PH
.313E-03	.244E-07	.782E-03	.719E-04	.923E-05	.1900E+00	.10E+00	.0146	43.9	6.56
.977E-03	.190E-06	.803E-03	.290E-04	.196E-04	.2129E-04	.17E-01	.0168	43.7	6.97
.907E-03	.100E-06	.827E-03	.514E-04	.186E-04	.1375E-08	.10E-01	.0206	43.5	6.73
.349E-03	.146E-07	.837E-03	.132E-03	.993E-05	.4260E-12	.59E-01	.0621	43.1	6.33
.152E-04	.339E-09	.843E-03	.237E-03	.125E-05	.4220E-14	.49E-01	.1199	42.6	6.07
.792E-07	.163E-11	.848E-03	.238E-03	.390E-07	.3644E-15	.28E-01	.1302	41.9	6.07
.231E-09	.470E-14	.852E-03	.220E-03	.829E-09	.4072E-16	.11E-01	.1346	41.0	6.10
.223E-11	.442E-16	.856E-03	.202E-03	.387E-10	.3771E-17	.35E-02	.1367	40.0	6.13
.102E-11	.195E-16	.859E-03	.186E-03	.231E-10	.2687E-18	.86E-03	.1375	38.9	6.17
.100E-11	.182E-16	.862E-03	.171E-03	.228E-10	.1577E-19	.22E-03	.1377	37.7	6.20
.100E-11	.172E-16	.865E-03	.158E-03	.228E-10	.9365E-21	.87E-04	.1375	36.5	6.22
.100E-11	.160E-16	.867E-03	.147E-03	.228E-10	.6969E-22	.59E-04	.1369	35.2	6.25
.100E-11	.148E-16	.869E-03	.138E-03	.228E-10	.5921E-23	.49E-04	.1362	34.0	6.27
.100E-11	.136E-16	.870E-03	.130E-03	.228E-10	.4706E-24	.42E-04	.1352	32.7	6.29
.100E-11	.124E-16	.870E-03	.123E-03	.228E-10	.9970E-26	.41E-04	.1343	31.4	6.31

% NH3-N LOSS = .1297E+02, % UREA HYDROLYZED = 93.54
 % N ACCOUNT= 99.7, % C ACCOUNT= 98.4, % H ACCOUNT= 100.0, % CA ACCOUNT= 97.9

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
1.05	21.1	24.8	29.0	29.9	28.3	.1	.0	.01484	.00	.00	509.	267.

DAY	HOURL	MIN
193	0	0

NH4AQ	NH3G	HC03	CO2G	NH4AD	UREA	CA	WA	TA	PH
.317E-03	.345E-08	.109E-02	.808E-04	.931E-05	.1341E+00	.10E+00	.0204	24.9	6.56
.971E-03	.290E-07	.110E-02	.322E-04	.195E-04	.2699E-04	.16E-01	.0214	25.5	6.96
.904E-03	.169E-07	.110E-02	.557E-04	.186E-04	.3605E-08	.24E-01	.0249	26.2	6.73
.351E-03	.273E-08	.110E-02	.143E-03	.995E-05	.1132E-11	.56E-01	.0509	26.8	6.32
.153E-04	.712E-10	.109E-02	.257E-03	.126E-05	.2552E-14	.46E-01	.1191	27.4	6.07
.796E-07	.394E-12	.109E-02	.260E-03	.392E-07	.1342E-16	.26E-01	.1262	28.0	6.06
.232E-09	.130E-14	.109E-02	.243E-03	.830E-09	.4985E-18	.11E-01	.1308	28.5	6.10
.223E-11	.142E-16	.108E-02	.225E-03	.387E-10	.5266E-19	.36E-02	.1335	29.0	6.13
.102E-11	.724E-17	.108E-02	.209E-03	.231E-10	.4978E-20	.94E-03	.1351	29.3	6.16
.100E-11	.783E-17	.108E-02	.195E-03	.228E-10	.4031E-21	.24E-03	.1359	29.6	6.19
.100E-11	.851E-17	.107E-02	.182E-03	.228E-10	.3047E-22	.93E-04	.1362	29.8	6.22
.100E-11	.913E-17	.107E-02	.172E-03	.228E-10	.2430E-23	.60E-04	.1360	29.9	6.25
.100E-11	.967E-17	.107E-02	.162E-03	.228E-10	.2169E-24	.49E-04	.1356	29.9	6.27
.100E-11	.101E-16	.107E-02	.155E-03	.228E-10	.2016E-25	.43E-04	.1349	29.9	6.29
.100E-11	.105E-16	.107E-02	.148E-03	.228E-10	.6213E-27	.41E-04	.1339	29.9	6.31

% NH3-N LOSS = .1308E+02, % UREA HYDROLYZED = 93.63
 % N ACCOUNT= 99.7, % C ACCOUNT= 98.4, % H ACCOUNT= 100.0, % CA ACCOUNT= 97.8

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
2.18	18.4	21.2	25.7	27.2	27.5	1.9	.5	.01350	.00	.00	147.	112.

DAY	HOUR	MIN
193	6	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.332E-03	.222E-08	.136E-02	.923E-04	.959E-05	.1045E+00	.10E+00	.0246	20.1	6.58
.969E-03	.164E-07	.139E-02	.399E-04	.195E-04	.2670E-04	.23E-01	.0247	20.6	6.95
.903E-03	.956E-08	.142E-02	.694E-04	.186E-04	.5415E-08	.38E-01	.0278	21.2	6.72
.351E-03	.155E-08	.143E-02	.178E-03	.996E-05	.2431E-11	.53E-01	.0538	21.7	6.32
.154E-04	.404E-10	.143E-02	.323E-03	.126E-05	.7351E-14	.44E-01	.1190	22.3	6.06
.801E-07	.225E-12	.144E-02	.328E-03	.393E-07	.3977E-16	.25E-01	.1253	22.9	6.06
.232E-09	.753E-15	.144E-02	.307E-03	.830E-09	.2581E-18	.11E-01	.1295	23.6	6.09
.223E-11	.832E-17	.144E-02	.286E-03	.387E-10	.5619E-20	.35E-02	.1321	24.1	6.13
.102E-11	.436E-17	.144E-02	.266E-03	.231E-10	.4131E-21	.93E-03	.1338	24.7	6.16
.100E-11	.485E-17	.144E-02	.249E-03	.228E-10	.3187E-22	.25E-03	.1348	25.2	6.19
.100E-11	.545E-17	.144E-02	.235E-03	.228E-10	.2276E-23	.94E-04	.1352	25.6	6.22
.100E-11	.606E-17	.144E-02	.222E-03	.228E-10	.1653E-24	.60E-04	.1351	26.1	6.24
.100E-11	.667E-17	.144E-02	.211E-03	.228E-10	.1316E-25	.49E-04	.1348	26.5	6.27
.100E-11	.728E-17	.144E-02	.202E-03	.228E-10	.1108E-26	.42E-04	.1341	26.8	6.29
.100E-11	.786E-17	.143E-02	.194E-03	.228E-10	.4750E-28	.41E-04	.1331	27.2	6.31

% NH3-N LOSS = .1310E+02, % UREA HYDROLYZED = 94.00
 % N ACCOUNT= 99.7, % C ACCOUNT= 98.5, % H ACCOUNT= 100.0, % CA ACCOUNT= 97.9

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
1.77	51.2	31.7	31.7	27.7	26.8	809.9	202.6	.01714	.00	.00	165.	95.

DAY	HOUR	MIN
193	12	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.338E-03	.390E-07	.117E-02	.110E-03	.971E-05	.1761E+00	.10E+00	.0140	47.6	6.58
.964E-03	.203E-06	.120E-02	.473E-04	.194E-04	.2717E-04	.19E-01	.0174	45.2	6.94
.901E-03	.904E-07	.124E-02	.800E-04	.186E-04	.2090E-08	.40E-01	.0237	42.9	6.71
.352E-03	.115E-07	.126E-02	.200E-03	.997E-05	.7217E-12	.50E-01	.0526	40.9	6.31
.154E-04	.227E-09	.129E-02	.352E-03	.127E-05	.1507E-13	.42E-01	.1163	38.8	6.06
.806E-07	.952E-12	.129E-02	.347E-03	.395E-07	.3016E-15	.25E-01	.1257	36.6	6.06
.232E-09	.246E-14	.130E-02	.317E-03	.831E-09	.4075E-17	.11E-01	.1300	34.8	6.09
.223E-11	.217E-16	.131E-02	.290E-03	.388E-10	.3804E-19	.36E-02	.1325	33.2	6.12
.102E-11	.937E-17	.132E-02	.266E-03	.231E-10	.2916E-21	.98E-03	.1340	31.9	6.16
.100E-11	.881E-17	.132E-02	.246E-03	.228E-10	.4579E-23	.26E-03	.1348	30.8	6.19
.100E-11	.856E-17	.133E-02	.229E-03	.228E-10	.2414E-24	.96E-04	.1351	29.9	6.22
.100E-11	.841E-17	.134E-02	.215E-03	.228E-10	.1634E-25	.60E-04	.1350	29.2	6.24
.100E-11	.832E-17	.134E-02	.203E-03	.228E-10	.1187E-26	.49E-04	.1345	28.6	6.27
.100E-11	.828E-17	.135E-02	.193E-03	.228E-10	.9115E-28	.42E-04	.1338	28.1	6.29
.100E-11	.827E-17	.135E-02	.184E-03	.228E-10	.4401E-29	.41E-04	.1328	27.7	6.31

% NH3-N LOSS = .1326E+02, % UREA HYDROLYZED = 94.23
 % N ACCOUNT= 99.7, % C ACCOUNT= 98.5, % H ACCOUNT= 100.0, % CA ACCOUNT= 97.7

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOOV	RAIN	RA	RH
4.66	40.4	35.0	35.8	31.8	28.0	412.8	102.9	.01678	.00	.00	95.	52.

DAY	HOUR	MIN
193	18	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.325E-03	.218E-07	.649E-03	.670E-04	.947E-05	.1697E+00	.10E+00	.0142	43.5	6.51
.937E-03	.166E-06	.679E-03	.263E-04	.190E-04	.2200E-04	.12E-01	.0157	43.4	6.94
.893E-03	.917E-07	.717E-03	.467E-04	.185E-04	.3317E-08	.20E-01	.0179	43.2	6.71
.357E-03	.141E-07	.732E-03	.119E-03	.101E-04	.1895E-12	.27E-01	.0216	42.9	6.31
.159E-04	.332E-09	.742E-03	.216E-03	.129E-05	.1501E-15	.38E-01	.0949	42.4	6.05
.828E-07	.159E-11	.750E-03	.218E-03	.402E-07	.3125E-17	.27E-01	.1224	41.6	6.05
.234E-09	.446E-14	.759E-03	.202E-03	.835E-09	.3936E-18	.13E-01	.1302	40.7	6.09
.223E-11	.419E-16	.768E-03	.186E-03	.388E-10	.3921E-19	.51E-02	.1339	39.8	6.12
.102E-11	.187E-16	.776E-03	.172E-03	.231E-10	.2874E-20	.15E-02	.1357	38.7	6.15
.100E-11	.176E-16	.784E-03	.159E-03	.228E-10	.1582E-21	.41E-03	.1366	37.7	6.18
.100E-11	.168E-16	.791E-03	.148E-03	.228E-10	.6682E-23	.13E-03	.1368	36.5	6.21
.100E-11	.159E-16	.797E-03	.138E-03	.228E-10	.2211E-24	.67E-04	.1365	35.3	6.24
.100E-11	.149E-16	.801E-03	.130E-03	.228E-10	.5860E-26	.51E-04	.1359	34.2	6.26
.100E-11	.138E-16	.805E-03	.122E-03	.228E-10	.1294E-27	.43E-04	.1351	33.0	6.29
.100E-11	.128E-16	.806E-03	.116E-03	.228E-10	.6455E-30	.41E-04	.1341	31.8	6.30

% NH3-N LOSS = .1422E+02, % UREA HYDROLYZED = 94.37

% N ACCOUNT= 99.7, % C ACCOUNT= 98.4, % H ACCOUNT= 100.0, % CA ACCOUNT= 97.3

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOOV	RAIN	RA	RH
1.16	21.0	24.9	27.6	29.7	28.7	-.1	.0	.01749	.00	.00	532.	440.

DAY	HOUR	MIN
194	0	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.359E-03	.282E-08	.104E-02	.897E-04	.101E-04	.3774E-02	.48E-01	.2007	23.4	6.49
.975E-03	.208E-07	.107E-02	.368E-04	.196E-04	.2754E-02	.70E-01	.1904	24.1	6.89
.914E-03	.143E-07	.107E-02	.552E-04	.187E-04	.1656E-02	.10E+00	.1224	24.8	6.71
.358E-03	.236E-08	.106E-02	.141E-03	.101E-04	.3814E-04	.36E-01	.0319	25.5	6.31
.161E-04	.628E-10	.106E-02	.254E-03	.130E-05	.3355E-07	.35E-01	.0915	26.1	6.05
.834E-07	.349E-12	.105E-02	.257E-03	.404E-07	.6264E-10	.25E-01	.1178	26.8	6.05
.234E-09	.113E-14	.105E-02	.238E-03	.836E-09	.1355E-12	.13E-01	.1261	27.4	6.08
.223E-11	.123E-16	.104E-02	.220E-03	.388E-10	.2748E-15	.50E-02	.1305	28.0	6.12
.102E-11	.640E-17	.103E-02	.204E-03	.231E-10	.5081E-18	.16E-02	.1330	28.4	6.15
.100E-11	.704E-17	.103E-02	.189E-03	.228E-10	.8571E-21	.44E-03	.1345	28.8	6.18
.100E-11	.780E-17	.102E-02	.177E-03	.228E-10	.1560E-23	.14E-03	.1351	29.1	6.21
.100E-11	.852E-17	.102E-02	.166E-03	.228E-10	.1536E-25	.70E-04	.1353	29.4	6.24
.100E-11	.918E-17	.102E-02	.156E-03	.228E-10	.6155E-27	.51E-04	.1351	29.6	6.26
.100E-11	.976E-17	.101E-02	.149E-03	.228E-10	.2396E-28	.43E-04	.1345	29.7	6.28
.100E-11	.103E-16	.101E-02	.142E-03	.228E-10	.3802E-30	.41E-04	.1335	29.7	6.30

% NH3-N LOSS = .1436E+02, % UREA HYDROLYZED = 96.55

% N ACCOUNT= 100.0, % C ACCOUNT= 99.0, % H ACCOUNT= 100.0, % CA ACCOUNT= 101.3

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
.98	18.6	19.5	24.7	26.6	27.6	.6	.2	.01614	.00	.00	313.	237.

DAY	HOUR	MIN
194	6	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.392E-03	.229E-08	.144E-02	.103E-03	.107E-04	.1883E-02	.44E-01	.1669	19.4	6.55
.101E-02	.120E-07	.149E-02	.569E-04	.200E-04	.1166E-02	.60E-01	.1631	20.1	6.82
.943E-03	.885E-08	.152E-02	.903E-04	.191E-04	.6006E-03	.97E-01	.1558	20.8	6.69
.360E-03	.151E-08	.152E-02	.194E-03	.101E-04	.1044E-03	.85E-01	.0577	21.4	6.31
.161E-04	.400E-10	.152E-02	.354E-03	.130E-05	.2386E-06	.33E-01	.0987	22.0	6.05
.836E-07	.222E-12	.152E-02	.358E-03	.404E-07	.8898E-09	.24E-01	.1163	22.7	6.05
.234E-09	.718E-15	.152E-02	.334E-03	.836E-09	.3716E-11	.12E-01	.1243	23.3	6.08
.223E-11	.785E-17	.152E-02	.310E-03	.388E-10	.1546E-13	.48E-02	.1289	23.9	6.11
.102E-11	.411E-17	.151E-02	.288E-03	.231E-10	.6221E-16	.15E-02	.1316	24.4	6.15
.100E-11	.456E-17	.151E-02	.268E-03	.228E-10	.2390E-18	.44E-03	.1332	24.8	6.18
.100E-11	.512E-17	.151E-02	.251E-03	.228E-10	.8701E-21	.14E-03	.1340	25.3	6.21
.100E-11	.568E-17	.151E-02	.236E-03	.225E-10	.2982E-23	.70E-04	.1343	25.7	6.24
.100E-11	.625E-17	.151E-02	.224E-03	.228E-10	.9612E-26	.51E-04	.1341	26.0	6.26
.100E-11	.680E-17	.150E-02	.213E-03	.228E-10	.3056E-28	.43E-04	.1335	26.3	6.28
.100E-11	.734E-17	.150E-02	.205E-03	.228E-10	.1306E-30	.42E-04	.1325	26.6	6.30

% NH3-N LOSS = .1437E+02, % UREA HYDROLYZED = 98.60
 % N ACCOUNT= 100.0, % C ACCOUNT= 99.1, % H ACCOUNT= 100.0, % CA ACCOUNT= 101.2

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
4.43	35.4	31.3	28.9	27.0	26.7	822.7	193.6	.01618	.00	.00	106.	57.

DAY	HOUR	MIN
194	12	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.416E-03	.142E-07	.130E-02	.104E-03	.111E-04	.9061E-03	.46E-01	.0246	35.3	6.58
.103E-02	.483E-07	.136E-02	.680E-04	.203E-04	.1466E-03	.55E-01	.1393	34.0	6.77
.952E-03	.301E-07	.147E-02	.956E-04	.193E-04	.7251E-04	.82E-01	.1368	32.8	6.65
.364E-03	.463E-08	.151E-02	.218E-03	.102E-04	.1774E-04	.10E+00	.0976	31.8	6.30
.162E-04	.105E-09	.153E-02	.395E-03	.131E-05	.3050E-06	.34E-01	.1033	31.0	6.04
.839E-07	.500E-12	.154E-02	.396E-03	.405E-07	.1417E-08	.23E-01	.1163	30.3	6.04
.235E-09	.141E-14	.155E-02	.369E-03	.836E-09	.7991E-11	.12E-01	.1237	29.7	6.07
.223E-11	.137E-16	.157E-02	.341E-03	.388E-10	.5063E-13	.48E-02	.1282	29.1	6.11
.102E-11	.645E-17	.158E-02	.316E-03	.231E-10	.3213E-15	.15E-02	.1310	28.6	6.14
.100E-11	.653E-17	.159E-02	.294E-03	.228E-10	.1981E-17	.44E-03	.1327	28.2	6.19
.100E-11	.673E-17	.160E-02	.275E-03	.228E-10	.1139E-19	.14E-03	.1335	27.9	6.21
.100E-11	.695E-17	.160E-02	.258E-03	.228E-10	.6016E-22	.70E-04	.1338	27.6	6.23
.100E-11	.717E-17	.161E-02	.244E-03	.228E-10	.2933E-24	.51E-04	.1336	27.3	6.26
.100E-11	.739E-17	.161E-02	.232E-03	.228E-10	.1331E-26	.42E-04	.1330	27.1	6.28
.100E-11	.761E-17	.162E-02	.222E-03	.228E-10	.4715E-29	.42E-04	.1320	27.0	6.30

% NH3-N LOSS = .1447E+02, % UREA HYDROLYZED = 99.88
 % N ACCOUNT= 99.9, % C ACCOUNT= 98.8, % H ACCOUNT= 100.0, % CA ACCOUNT= 100.2

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOOV	RAIN	RA	RH
5.01	35.1	31.8	33.5	30.5	27.4	325.4	81.0	.01681	.00	.00	93.	50.

DAY	HOUR	MIN
194	18	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.391E-03	.146E-07	.676E-03	.657E-04	.107E-04	.6899E-03	.33E-01	.0160	37.7	6.51
.102E-02	.688E-07	.710E-03	.397E-04	.202E-04	.2947E-06	.48E-01	.0546	38.1	6.75
.950E-03	.491E-07	.762E-03	.563E-04	.192E-04	.8817E-07	.68E-01	.1153	38.2	6.63
.366E-03	.865E-08	.793E-03	.126E-03	.102E-04	.3379E-07	.99E-01	.1127	38.1	6.29
.164E-04	.210E-09	.808E-03	.229E-03	.132E-05	.5519E-08	.47E-01	.1109	37.7	6.04
.851E-07	.103E-11	.818E-03	.231E-03	.409E-07	.3855E-09	.25E-01	.1176	37.2	6.04
.235E-09	.288E-14	.828E-03	.215E-03	.838E-09	.1667E-10	.13E-01	.1240	36.6	6.07
.223E-11	.275E-16	.837E-03	.199E-03	.388E-10	.5352E-12	.52E-02	.1284	35.9	6.11
.102E-11	.126E-16	.846E-03	.184E-03	.231E-10	.1343E-13	.18E-02	.1312	35.2	6.14
.100E-11	.124E-16	.855E-03	.171E-03	.228E-10	.2698E-15	.52E-03	.1329	34.4	6.17
.100E-11	.123E-16	.863E-03	.160E-03	.228E-10	.4425E-17	.16E-03	.1338	33.6	6.20
.100E-11	.121E-16	.869E-03	.149E-03	.228E-10	.6018E-19	.75E-04	.1341	32.9	6.23
.100E-11	.118E-16	.874E-03	.141E-03	.228E-10	.6895E-21	.52E-04	.1339	32.1	6.26
.100E-11	.114E-16	.878E-03	.133E-03	.228E-10	.6752E-23	.43E-04	.1332	31.3	6.28
.100E-11	.110E-16	.880E-03	.126E-03	.228E-10	.1677E-25	.42E-04	.1323	30.5	6.30

% NH3-N LOSS = .1521E+02, % UREA HYDROLYZED = 99.97

% N ACCOUNT= 99.8, % C ACCOUNT= 98.7, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.6

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOOV	RAIN	RA	RH
3.27	22.3	25.8	27.9	29.1	28.2	.1	.0	.01706	.00	.00	88.	66.

DAY	HOUR	MIN
195	0	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.388E-03	.363E-08	.630E-03	.548E-04	.106E-04	.1884E-03	.55E-01	.0233	24.9	6.49
.102E-02	.177E-07	.660E-03	.326E-04	.202E-04	.6741E-07	.45E-01	.0359	25.4	6.74
.949E-03	.129E-07	.699E-03	.472E-04	.192E-04	.2916E-08	.69E-01	.1099	25.9	6.60
.367E-03	.253E-08	.722E-03	.102E-03	.103E-04	.8728E-09	.97E-01	.1117	26.5	6.28
.165E-04	.684E-10	.733E-03	.184E-03	.132E-05	.1338E-09	.46E-01	.1133	27.0	6.04
.855E-07	.371E-12	.740E-03	.188E-03	.410E-07	.1107E-10	.24E-01	.1179	27.4	6.04
.236E-09	.115E-14	.746E-03	.176E-03	.839E-09	.6145E-12	.12E-01	.1228	27.8	6.07
.223E-11	.123E-16	.752E-03	.164E-03	.388E-10	.2587E-13	.52E-02	.1267	28.2	6.10
.102E-11	.625E-17	.757E-03	.153E-03	.231E-10	.8893E-15	.18E-02	.1295	28.5	6.14
.100E-11	.678E-17	.761E-03	.143E-03	.228E-10	.2603E-16	.53E-03	.1314	28.7	6.17
.100E-11	.740E-17	.765E-03	.134E-03	.228E-10	.6700E-18	.17E-03	.1325	28.9	6.20
.100E-11	.799E-17	.768E-03	.127E-03	.228E-10	.1558E-19	.77E-04	.1330	29.0	6.23
.100E-11	.854E-17	.770E-03	.120E-03	.228E-10	.3355E-21	.53E-04	.1329	29.0	6.25
.100E-11	.901E-17	.771E-03	.114E-03	.228E-10	.6819E-23	.43E-04	.1324	29.1	6.28
.100E-11	.942E-17	.772E-03	.109E-03	.228E-10	.6747E-25	.42E-04	.1315	29.1	6.30

% NH3-N LOSS = .1536E+02, % UREA HYDROLYZED = 99.99

% N ACCOUNT= 99.8, % C ACCOUNT= 98.7, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.5

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOCV	RAIN	RA	RH
.98	20.8	23.5	24.7	26.6	27.6	.6	.2	.01768	.00	.00	733.	616.

DAY	HOUR	MIN
195	6	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.387E-03	.267E-08	.728E-03	.626E-04	.106E-04	.1884E-03	.68E-01	.0302	22.3	6.48
.102E-02	.129E-07	.736E-03	.364E-04	.201E-04	.6741E-07	.45E-01	.0368	22.7	6.72
.949E-03	.901E-08	.744E-03	.516E-04	.192E-04	.2916E-08	.70E-01	.1074	23.2	6.58
.367E-03	.182E-08	.748E-03	.105E-03	.103E-04	.8728E-09	.94E-01	.1116	23.6	6.27
.165E-04	.497E-10	.749E-03	.184E-03	.133E-05	.1338E-09	.45E-01	.1148	24.1	6.03
.858E-07	.269E-12	.750E-03	.186E-03	.411E-07	.1107E-10	.23E-01	.1188	24.5	6.03
.236E-09	.833E-15	.751E-03	.173E-03	.839E-09	.6145E-12	.12E-01	.1228	24.9	6.07
.223E-11	.887E-17	.751E-03	.160E-03	.388E-10	.2587E-13	.50E-02	.1261	25.3	6.10
.102E-11	.455E-17	.752E-03	.149E-03	.231E-10	.8893E-15	.17E-02	.1287	25.6	6.14
.100E-11	.497E-17	.752E-03	.138E-03	.228E-10	.2603E-16	.53E-03	.1304	25.9	6.17
.100E-11	.549E-17	.752E-03	.129E-03	.228E-10	.6700E-18	.17E-03	.1315	26.1	6.20
.100E-11	.600E-17	.752E-03	.121E-03	.228E-10	.1558E-19	.77E-04	.1320	26.4	6.23
.100E-11	.650E-17	.752E-03	.114E-03	.228E-10	.3355E-21	.52E-04	.1320	26.5	6.25
.100E-11	.695E-17	.752E-03	.109E-03	.228E-10	.6819E-23	.43E-04	.1315	26.7	6.28
.100E-11	.725E-17	.752E-03	.104E-03	.228E-10	.6747E-25	.42E-04	.1305	26.6	6.30

% NH3-N LOSS = .1543E+02, % UREA HYDROLYZED = 99.99
 % N ACCOUNT= 99.8, % C ACCOUNT= 98.7, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.5

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDOCV	RAIN	RA	RH
4.43	35.4	31.3	28.9	27.0	26.7	822.7	193.6	.01618	.00	.00	94.	51.

DAY	HOUR	MIN
195	12	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.383E-03	.247E-07	.711E-03	.823E-04	.106E-04	.1884E-03	.79E-01	.0143	44.2	6.47
.101E-02	.980E-07	.739E-03	.473E-04	.201E-04	.6741E-07	.36E-01	.0188	42.5	6.71
.948E-03	.527E-07	.780E-03	.699E-04	.192E-04	.2916E-08	.66E-01	.0969	40.6	6.56
.367E-03	.848E-08	.810E-03	.139E-03	.103E-04	.8728E-09	.92E-01	.1126	38.5	6.26
.166E-04	.186E-09	.827E-03	.237E-03	.133E-05	.1338E-09	.49E-01	.1171	36.7	6.03
.964E-07	.818E-12	.838E-03	.236E-03	.413E-07	.1107E-10	.24E-01	.1207	35.1	6.03
.236E-09	.209E-14	.849E-03	.218E-03	.840E-09	.6145E-12	.12E-01	.1240	33.6	6.06
.223E-11	.188E-16	.860E-03	.200E-03	.388E-10	.2587E-13	.51E-02	.1267	32.4	6.10
.102E-11	.828E-17	.870E-03	.184E-03	.231E-10	.8893E-15	.18E-02	.1289	31.3	6.13
.100E-11	.793E-17	.879E-03	.171E-03	.228E-10	.2603E-16	.55E-03	.1304	30.3	6.17
.100E-11	.779E-17	.886E-03	.159E-03	.228E-10	.6700E-18	.17E-03	.1312	29.4	6.20
.100E-11	.770E-17	.893E-03	.148E-03	.228E-10	.1558E-19	.78E-04	.1316	28.7	6.23
.100E-11	.763E-17	.898E-03	.140E-03	.228E-10	.3355E-21	.53E-04	.1315	28.1	6.25
.100E-11	.758E-17	.902E-03	.132E-03	.228E-10	.6819E-23	.43E-04	.1309	27.5	6.27
.100E-11	.752E-17	.904E-03	.126E-03	.228E-10	.6747E-25	.42E-04	.1300	27.0	6.29

% NH3-N LOSS = .1558E+02, % UREA HYDROLYZED = 99.99
 % N ACCOUNT= 99.8, % C ACCOUNT= 98.7, % H ACCOUNT= 100.0, % CA ACCOUNT= 99.2

UHM	TSURF	TAIR	T6CM	T15CM	T30CM	SW	RESW	VDA	CLDCOV	RAIN	RA	RH
5.01	35.1	31.8	33.5	30.5	27.4	325.4	81.0	.01681	.00	.00	92.	50.

DAY	HOUR	MIN
195	18	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.366E-03	.120E-07	.417E-03	.512E-04	.102E-04	.1894E-03	.99E-01	.0154	38.7	6.41
.100E-02	.677E-07	.436E-03	.268E-04	.199E-04	.6741E-07	.19E-02	.0195	39.0	6.71
.945E-03	.444E-07	.457E-03	.410E-04	.192E-04	.2916E-08	.58E-01	.0388	39.1	6.55
.369E-03	.880E-08	.471E-03	.825E-04	.103E-04	.8728E-09	.85E-01	.1065	39.0	6.26
.169E-04	.228E-09	.480E-03	.142E-03	.135E-05	.1338E-09	.53E-01	.1167	38.6	6.03
.880E-07	.113E-11	.486E-03	.143E-03	.418E-07	.1107E-10	.28E-01	.1217	38.1	6.03
.237E-09	.307E-14	.491E-03	.133E-03	.843E-09	.6145E-12	.14E-01	.1252	37.5	6.06
.223E-11	.290E-16	.497E-03	.123E-03	.388E-10	.2587E-13	.60E-02	.1278	36.7	6.09
.102E-11	.133E-16	.501E-03	.113E-03	.231E-10	.8893E-15	.22E-02	.1297	35.9	6.13
.100E-11	.129E-16	.506E-03	.104E-03	.228E-10	.2603E-16	.68E-03	.1311	35.0	6.16
.100E-11	.126E-16	.510E-03	.969E-04	.228E-10	.6700E-18	.21E-03	.1319	34.1	6.19
.100E-11	.123E-16	.513E-03	.903E-04	.228E-10	.1558E-19	.88E-04	.1321	33.2	6.22
.100E-11	.119E-16	.516E-03	.845E-04	.228E-10	.3355E-21	.55E-04	.1320	32.3	6.25
.100E-11	.114E-16	.517E-03	.796E-04	.228E-10	.6819E-23	.44E-04	.1314	31.4	6.27
.100E-11	.109E-16	.518E-03	.751E-04	.228E-10	.6747E-25	.42E-04	.1304	30.5	6.29

% NH3-N LOSS = .1623E+02, % UREA HYDROLYZED = 99.99

% N ACCOUNT= 99.7, % C ACCOUNT= 98.7, % H ACCOUNT= 100.0, % CA ACCOUNT= 98.7

DAY	HOUR	MIN
195	20	0

NH4AQ	NH3G	HCO3	CO2G	NH4AD	UREA	CA	WA	TA	PH
.365E-03	.583E-08	.454E-03	.522E-04	.102E-04	.1884E-03	.10E+00	.0173	31.8	6.40
.999E-03	.344E-07	.467E-03	.265E-04	.199E-04	.6741E-07	.83E-02	.0208	32.4	6.71
.944E-03	.234E-07	.479E-03	.399E-04	.191E-04	.2916E-08	.58E-01	.0321	32.8	6.55
.370E-03	.491E-08	.486E-03	.796E-04	.103E-04	.8728E-09	.84E-01	.1054	33.3	6.25
.169E-04	.137E-09	.489E-03	.137E-03	.135E-05	.1338E-09	.53E-01	.1156	33.6	6.02
.882E-07	.730E-12	.492E-03	.138E-03	.419E-07	.1107E-10	.28E-01	.1209	33.8	6.02
.237E-09	.214E-14	.493E-03	.128E-03	.843E-09	.6145E-12	.14E-01	.1245	33.9	6.06
.223E-11	.216E-16	.495E-03	.118E-03	.388E-10	.2587E-13	.60E-02	.1273	33.8	6.09
.102E-11	.105E-16	.496E-03	.109E-03	.231E-10	.8893E-15	.22E-02	.1293	33.6	6.13
.100E-11	.108E-16	.497E-03	.101E-03	.228E-10	.2603E-16	.70E-03	.1307	33.3	6.16
.100E-11	.111E-16	.497E-03	.933E-04	.228E-10	.6700E-18	.22E-03	.1316	32.9	6.19
.100E-11	.113E-16	.498E-03	.869E-04	.228E-10	.1558E-19	.90E-04	.1319	32.4	6.22
.100E-11	.114E-16	.498E-03	.814E-04	.228E-10	.3355E-21	.56E-04	.1318	31.9	6.25
.100E-11	.113E-16	.498E-03	.766E-04	.228E-10	.6819E-23	.44E-04	.1313	31.4	6.27
.100E-11	.112E-16	.498E-03	.726E-04	.228E-10	.6747E-25	.42E-04	.1303	30.8	6.29

% NH3-N LOSS = .1630E+02, % UREA HYDROLYZED = 99.99

% N ACCOUNT= 99.7, % C ACCOUNT= 98.7, % H ACCOUNT= 100.0, % CA ACCOUNT= 98.7

Table 2. Modeled urea hydrolyzed, ammonia-N loss and ammonia-N flux

JULIAN TIME day:hour	UREA HYDROL %	UREA UNHYDROL %	NH ₃ -N LOSS %	NH ₃ -N FLUX ug/(m ²)(s)	AVERAGE JULIAN TIME day:hour
180:20	0.00	100.00	0.00	0.000E+00	180:16
181:0	1.25	98.75	0.00	4.167E-04	180:22
	2.85	97.15	0.00	8.333E-04	181:3
	5.01	94.99	0.00	9.772E-03	
	5.61	94.39	0.12	6.797E-01	
182:0	5.94	94.06	0.15	1.306E-01	
	6.58	93.42	0.17	1.306E-01	182:3
	7.05	92.95	0.23	3.244E-01	
	7.18	92.82	0.47	1.328E+00	
183:0	7.58	92.42	0.53	3.278E-01	
	8.40	91.60	0.56	1.972E-01	183:3
	8.86	91.14	0.67	5.817E-01	
	8.99	91.01	1.03	2.034E+00	
184:0	9.44	90.56	1.12	4.500E-01	
	10.20	89.80	1.21	5.111E-01	184:3
	10.50	89.50	1.42	1.189E+00	
	10.63	89.37	1.96	2.967E+00	
185:0	10.84	89.16	2.05	5.333E-01	
	11.17	88.83	2.07	1.056E-01	185:3
	12.56	87.44	2.09	1.167E-01	
	13.00	87.00	2.43	1.883E+00	
186:0	13.17	86.83	2.48	2.722E-01	
	13.59	86.41	2.48	2.222E-02	186:3
	14.13	85.87	2.57	4.611E-01	
	14.29	85.71	2.98	2.283E+00	
187:0	17.97	82.03	3.03	2.833E-01	
	22.73	77.27	3.04	5.000E-02	187:3
	31.28	68.72	3.17	7.167E-01	
	49.58	50.42	4.23	5.883E+00	
188:0	56.59	43.41	4.39	9.111E-01	
	59.76	40.24	4.40	7.778E-02	188:3
	64.04	35.96	4.74	1.883E+00	
	66.19	33.81	6.01	7.017E+00	
189:0	66.44	33.56	6.20	1.100E+00	
	68.89	33.11	6.26	2.944E-01	189:3
	67.20	32.80	6.58	1.794E+00	
	67.32	32.68	7.70	6.233E+00	
190:0	70.42	29.58	7.85	8.333E-01	
	74.91	25.09	7.88	1.333E-01	190:3
	81.73	18.27	8.05	9.944E-01	
	91.31	8.69	9.38	7.350E+00	
191:0	91.78	8.22	9.57	1.078E+00	
	92.21	7.79	9.59	8.333E-02	191:3
	92.51	7.49	9.94	1.950E+00	
	92.63	7.37	11.29	7.517E+00	
192:0	92.73	7.27	11.50	1.167E+00	
	93.11	6.89	11.56	3.333E-01	192:3
	93.40	6.60	11.83	1.500E+00	
	93.54	6.46	12.97	6.333E+00	
193:0	93.63	6.37	13.08	6.111E-01	
	94.00	6.00	13.10	1.111E-01	193:3
	94.23	5.77	13.26	8.889E-01	
	94.37	5.63	14.22	9.333E+00	
194:0	96.55	3.45	14.36	7.778E-01	
	98.60	1.40	14.37	5.556E-02	194:3
	99.88	0.12	14.47	5.556E-01	
	99.97	0.03	15.21	4.111E+00	
195:0	99.99	0.01	15.36	8.333E-01	
	99.99	0.01	15.43	3.889E-01	195:3
	99.99	0.01	15.58	8.333E-01	
195:18	99.99	0.01	16.23	3.611E+00	195:15
195:20	99.99	0.01	16.30	1.167E+00	195:19

Table 3. Modeled distribution of urea and soil water prior to and after the first irrigation

Julian Day:Hour = 186:18

DEPTH INTERVAL cm	WA m^3/m^3	UREA $\text{kmol}/\text{m}^3 \text{ soil}$	UREA $\text{kmol}/\text{m}^2 \text{ soil}$	UREA %
0-1	0.0135	2.711E+00	3.661E-04	99.98
1-2	0.0161	5.362E-04	8.633E-08	0.02
2-3	0.0201	5.410E-08	1.087E-11	0.00
3-4	0.0400	8.747E-12	3.499E-15	0.00
4-5	0.1165	1.893E-13	2.205E-16	0.00
5-6	0.1304	1.752E-14	2.285E-17	0.00
6-7	0.1375	1.537E-15	2.113E-18	0.00
7-8	0.1417	1.039E-16	1.472E-19	0.00
8-9	0.1443	5.480E-18	7.908E-21	0.00
9-10	0.1457	2.418E-19	3.523E-22	0.00
			3.662E-04	100.00

Julian Day:Hour = 187:18

DEPTH INTERVAL cm	WA m^3/m^3	UREA $\text{kmol}/\text{m}^3 \text{ soil}$	UREA $\text{kmol}/\text{m}^2 \text{ soil}$	UREA %
0-1	0.0151	7.276E-01	1.099E-04	50.78
1-2	0.0514	1.071E-01	5.505E-05	25.44
2-3	0.1239	3.056E-02	3.796E-05	17.50
3-4	0.1302	1.003E-02	1.306E-05	6.04
4-5	0.1320	3.895E-04	5.141E-07	0.24
5-6	0.1335	1.533E-05	2.047E-08	0.01
6-7	0.1358	5.064E-07	6.877E-10	0.00
7-8	0.1382	1.316E-08	1.819E-11	0.00
8-9	0.1402	2.741E-10	3.843E-13	0.00
9-10	0.1416	4.662E-12	6.601E-15	0.00
			2.164E-04	100.00

Table 4. Modeled distribution of ammonium corresponding to last field measurement

DEPTH INTERVAL	NH4AQ	WA	BD	NH4AD	TOTAL NH4-N	NH4-N
cm	kmol/m ³ soil	m ³ /m ³	Mg/m ³	mol/kg soil	kmol/kg soil	%
0-1	3.25E-04	0.0142	1.155	9.47E-06	9.47E-06	16.2
1-2	9.37E-04	0.0157	1.165	1.90E-05	1.90E-05	32.5
2-3	8.93E-04	0.0179	1.175	1.85E-05	1.85E-05	31.7
3-4	3.57E-04	0.0206	1.185	1.01E-05	1.01E-05	17.3
4-5	1.59E-05	0.0949	1.195	1.29E-06	1.29E-06	2.2
5-6	8.28E-08	0.1224	1.205	4.02E-08	4.02E-08	0.1
6-7	2.34E-10	0.1302	1.215	8.35E-10	8.35E-10	0.0
7-8	2.23E-12	0.1339	1.225	3.88E-11	3.88E-11	0.0
8-9	1.02E-12	0.1357	1.235	2.31E-11	2.31E-11	0.0
9-10	1.00E-12	0.1366	1.245	2.28E-11	2.28E-11	0.0
				SUM =	5.84E-05	100.0

Table 5. Modeled soil surface pH and CO₂ and NH₃ concentrations

JULIAN TIME day:hour	TEMP deg. C	pH	CO ₂ CONCENTRATION		NH ₃ CONCENTRATION	
			kmol/m ³	atm	kmol/m ³	mm Hg
180:20	27.3	6.40	1.42E-04	0.0035	9.86E-18	1.85E-13
181:0	21.3	6.44	8.22E-05	0.0020	4.15E-11	7.62E-07
	18.2	6.49	1.19E-04	0.0028	1.00E-10	1.82E-06
	42.9	6.56	8.86E-05	0.0023	2.38E-09	4.69E-05
	42.2	6.57	5.00E-05	0.0013	2.29E-09	4.50E-05
182:0	26.5	6.59	4.99E-05	0.0012	5.48E-10	1.02E-05
	23.7	6.65	3.92E-05	0.0010	5.87E-10	1.09E-05
	44.6	6.67	5.11E-05	0.0013	5.94E-09	1.18E-04
	42.5	6.66	4.16E-05	0.0011	4.56E-09	8.98E-05
183:0	27.8	6.68	3.69E-05	0.0009	1.19E-09	2.23E-05
	22.9	6.73	4.06E-05	0.0010	9.91E-10	1.83E-05
	41.8	6.75	4.61E-05	0.0012	7.91E-09	1.55E-04
	37.5	6.72	3.81E-05	0.0010	4.48E-09	8.68E-05
184:0	27.6	6.74	3.78E-05	0.0009	1.84E-09	3.45E-05
	25.7	6.77	3.09E-05	0.0008	1.89E-09	3.52E-05
	43.9	6.76	4.01E-05	0.0010	1.18E-08	2.33E-04
	45.7	6.71	4.34E-05	0.0011	1.12E-08	2.23E-04
185:0	24.9	6.72	4.74E-05	0.0012	1.39E-09	2.58E-05
	21.1	6.74	5.55E-05	0.0013	1.04E-09	1.91E-05
	34.5	6.79	7.53E-05	0.0019	6.10E-09	1.17E-04
	41.5	6.78	7.04E-05	0.0018	1.11E-08	2.18E-04
186:0	20.2	6.78	7.20E-05	0.0017	1.20E-09	2.20E-05
	15.6	6.80	8.64E-05	0.0020	7.95E-10	1.43E-05
	44.5	6.82	1.08E-04	0.0028	1.81E-08	3.59E-04
	43.1	6.80	9.04E-05	0.0023	1.42E-08	2.80E-04
187:0	18.8	6.92	7.33E-05	0.0018	1.92E-09	3.50E-05
	14.8	7.00	7.80E-05	0.0018	1.82E-09	3.27E-05
	33.4	7.04	1.03E-04	0.0026	2.09E-08	4.00E-04
	38.3	6.94	1.37E-04	0.0035	2.40E-08	4.66E-04
188:0	20.4	6.96	1.21E-04	0.0029	3.81E-09	6.98E-05
	17.0	7.00	1.25E-04	0.0030	3.02E-09	5.46E-05
	43.1	7.00	1.44E-04	0.0037	4.77E-08	9.41E-04
	39.7	6.89	1.11E-04	0.0028	2.35E-08	4.59E-04
189:0	22.9	6.90	8.36E-05	0.0020	4.16E-09	7.68E-05
	19.1	6.94	7.50E-05	0.0018	3.20E-09	5.83E-05
	43.6	6.92	9.02E-05	0.0023	3.95E-08	7.80E-04
	40.7	6.81	7.41E-05	0.0019	2.07E-08	4.05E-04
190:0	20.0	6.88	6.29E-05	0.0015	3.21E-09	5.87E-05
	16.4	6.93	8.12E-05	0.0019	2.81E-09	5.07E-05
	39.2	6.92	1.11E-04	0.0028	3.92E-08	7.64E-04
	39.4	6.79	1.13E-04	0.0029	2.63E-08	5.13E-04
191:0	22.4	6.79	9.89E-05	0.0024	4.45E-09	8.20E-05
	17.6	6.81	1.11E-04	0.0026	2.88E-09	5.22E-05
	45.1	6.79	1.16E-04	0.0030	4.97E-08	9.86E-04
	41.2	6.67	7.96E-05	0.0021	2.37E-08	4.65E-04
192:0	23.7	6.65	6.42E-05	0.0016	3.71E-09	6.87E-05
	20.5	6.67	6.98E-05	0.0017	2.83E-09	5.18E-05
	46.6	6.65	8.42E-05	0.0022	4.07E-08	8.12E-04
	43.9	6.56	7.19E-05	0.0019	2.44E-08	4.82E-04
193:0	24.9	6.56	8.08E-05	0.0020	3.45E-09	6.41E-05
	20.1	6.58	9.23E-05	0.0022	2.22E-09	4.06E-05
	47.6	6.58	1.10E-04	0.0029	3.90E-08	7.80E-04
	43.5	6.51	6.70E-05	0.0017	2.18E-08	4.31E-04
194:0	23.4	6.49	8.97E-05	0.0022	2.82E-09	5.22E-05
	19.4	6.55	1.03E-04	0.0025	2.29E-09	4.19E-05
	35.3	6.58	1.04E-04	0.0026	1.42E-08	2.73E-04
	37.7	6.51	6.57E-05	0.0017	1.46E-08	2.83E-04
195:0	24.9	6.49	5.48E-05	0.0013	3.63E-09	6.75E-05
	22.3	6.48	6.26E-05	0.0015	2.67E-09	4.92E-05
	44.2	6.47	8.23E-05	0.0021	2.47E-08	4.89E-04
195:18	38.7	6.41	5.12E-05	0.0013	1.20E-08	2.33E-04
195:20	31.8	6.40	5.22E-05	0.0013	5.83E-09	1.11E-04

Table 6. Modeled initial and final soil surface pH and soil water content

DEPTH INTERVAL cm	WA m^3/m^3		pH		H^+ $kmol/m^2$		CHANGE
	Initial	Final	Initial	Final	Initial	Final	%
0-1	0.0576	0.0173	6.40	6.40	2.29E-10	6.89E-11	-70.0
1-2	0.0757	0.0208	6.40	6.71	3.01E-10	4.06E-11	-86.5
2-3	0.0928	0.0321	6.40	6.55	3.69E-10	9.05E-11	-75.5
3-4	0.1091	0.1054	6.40	6.25	4.34E-10	5.93E-10	36.5
4-5	0.1243	0.1156	6.40	6.02	4.95E-10	1.10E-09	123.1
5-6	0.1387	0.1209	6.40	6.02	5.52E-10	1.15E-09	109.1
6-7	0.1520	0.1245	6.40	6.06	6.05E-10	1.08E-09	79.2
7-8	0.1643	0.1273	6.40	6.09	6.54E-10	1.03E-09	58.2
8-9	0.1755	0.1293	6.40	6.13	6.99E-10	9.59E-10	37.2
9-10	0.1856	0.1307	6.40	6.16	7.39E-10	9.04E-10	22.4
10-11	0.1946	0.1316	6.40	6.19	7.75E-10	8.50E-10	9.7
11-12	0.2024	0.1319	6.40	6.22	8.06E-10	7.95E-10	-1.4
12-13	0.2090	0.1318	6.40	6.25	8.32E-10	7.41E-10	-10.9
13-14	0.2139	0.1313	6.40	6.27	8.52E-10	7.05E-10	-17.2
14-15	0.2189	0.1303	6.40	6.29	8.71E-10	6.68E-10	-23.3
SUM =					9.21E-09	1.08E-08	17.1

Table 7. Modeled results for sensitivity analysis

PARAMETER	VALUE	UREA HYDROL %	NH ₃ -N LOSS %	SURFACE pH MAXIMUM MINIMUM	PERCENT N C Ca II	RECOVERED
STANDARD*						
INITIAL pH		99.99	16.30	7.04	99.7	98.7
INITIAL pH	6.0	99.99	12.31	6.71	99.7	98.5
TOTAL Ca ²⁺ , mg/kg	7.0	99.99	20.06	7.33	99.7	98.3
TOTAL Ca ²⁺ , mg/kg	900	99.99	16.30	7.04	99.7	98.3
ORGANIC CARBON, %	3600	99.99	16.30	7.04	99.7	97.4
ORGANIC CARBON, %	0.52	97.68	13.43	7.18	99.7	99.3
ORGANIC CARBON, %	2.08	99.99	19.53	6.91	99.7	98.5
APPLIED UREA-N, kg/ha	60	99.99	25.50	7.03	99.6	98.8
APPLIED UREA-N, kg/ha	240	95.52	10.01	7.04	99.8	100.9
SOIL RESP. RATE, kmol/(m ³)(s)	1.4E-08	99.99	13.59	6.90	99.7	94.6
SOIL RESP. RATE, kmol/(m ³)(s)	5.6E-08	99.99	22.76	7.31	99.7	98.5
FREUNDLICH EQN. COEFFICIENT	9.5E-04	99.99	18.24	6.75	100.2	99.0
FREUNDLICH EQN. COEFFICIENT	3.8E-03	99.99	14.68	7.32	99.9	98.4
CO ₂ SOLUB. CORRECTION FACTOR	5	99.99	12.82	6.89	99.7	99.3
CO ₂ SOLUB. CORRECTION FACTOR	20	99.99	22.97	7.28	99.7	98.8
NH ₃ SOLUB. CORRECTION FACTOR	5	99.99	8.62	6.97	99.7	98.3
NH ₃ SOLUB. CORRECTION FACTOR	20	99.99	29.18	7.18	99.7	98.5
SOIL BUFFER CAPACITY FACTOR	0.5	99.99	15.72	7.13	99.7	99.4
SOIL BUFFER CAPACITY FACTOR	2.0	99.99	16.00	6.87	99.7	98.7
FRAC. CO ₂ RESIST. IN GAS FILM	0.0025	99.99	15.39	6.94	99.7	98.5
FRAC. CO ₂ RESIST. IN GAS FILM	0.0100	99.99	17.42	7.13	99.7	98.7
IRRIGATION DEPTHS, cm	0.25	78.90	16.49	7.02	99.8	97.1
IRRIGATION DEPTHS, cm	1.00	99.99	13.20	7.04	99.9	105.6
SINGLE IRRIGATION, cm	2.54	99.99	7.28	7.56	99.7	98.1

*See Table 1 for STANDARD parameter values

Table 8. Modeled surface soil water content and measured and modeled surface soil temperature

JULIAN TIME day:hour	WATER CONTENT		SURFACE TEMPERATURE	
	m ³ /m ³	kg/kg	Measured deg. C	Modeled deg. C
180:20	0.0576	0.0499	27.0	27.3
181:0	0.0537	0.0465	19.4	21.3
	0.0564	0.0488	17.4	18.2
	0.0148	0.0128	43.0	42.9
	0.0150	0.0130	39.5	42.2
182:0	0.0239	0.0207	23.7	26.5
	0.0257	0.0223	20.9	23.7
	0.0146	0.0126	45.7	44.6
	0.0153	0.0132	40.6	42.5
183:0	0.0236	0.0204	25.1	27.6
	0.0272	0.0235	20.4	22.9
	0.0154	0.0133	43.8	41.8
	0.0169	0.0146	34.9	37.5
184:0	0.0243	0.0210	25.5	27.6
	0.0240	0.0208	23.7	25.7
	0.0144	0.0125	45.0	43.9
	0.0137	0.0119	43.8	45.7
185:0	0.0231	0.0200	21.1	24.9
	0.0214	0.0185	20.0	21.1
	0.0174	0.0151	35.5	34.5
	0.0136	0.0118	38.8	41.5
186:0	0.0209	0.0181	15.7	20.2
	0.0256	0.0222	14.2	15.6
	0.0135	0.0117	48.2	44.5
	0.0135	0.0117	40.6	43.1
187:0	0.1969	0.1705	16.6	18.8
	0.1699	0.1471	14.1	14.8
	0.0260	0.0225	35.8	33.4
	0.0151	0.0131	35.2	38.3
188:0	0.0241	0.0209	16.5	20.4
	0.0297	0.0257	14.7	17.0
	0.0142	0.0123	44.1	43.1
	0.0146	0.0126	37.1	39.7
189:0	0.0220	0.0190	19.6	22.9
	0.0268	0.0232	16.4	19.1
	0.0141	0.0122	45.2	43.6
	0.0141	0.0122	36.9	40.7
190:0	0.1929	0.1670	17.7	20.0
	0.1613	0.1397	14.7	16.4
	0.0157	0.0136	37.5	39.2
	0.0150	0.0130	36.8	39.4
191:0	0.0225	0.0195	18.1	22.4
	0.0275	0.0238	14.9	17.6
	0.0139	0.0120	46.0	45.1
	0.0145	0.0126	38.1	41.2
192:0	0.0205	0.0177	21.0	23.7
	0.0252	0.0218	17.4	20.5
	0.0138	0.0119	48.1	46.6
	0.0146	0.0126	41.1	43.9
193:0	0.0204	0.0177	21.1	24.9
	0.0246	0.0213	18.4	20.1
	0.0140	0.0121	51.2	47.6
	0.0142	0.0123	40.4	43.5
194:0	0.2007	0.1738	21.0	23.4
	0.1669	0.1445	18.6	19.4
	0.0246	0.0213	35.4	35.3
	0.0160	0.0139	35.1	37.7
195:0	0.0233	0.0202	22.3	24.9
	0.0302	0.0261	20.8	22.3
	0.0143	0.0124	35.4	44.2
	0.0154	0.0133	35.1	38.7
195:20	0.0173	0.0150	30.9	31.8

Table 9. Sample of input file for meteorological data, FILE: WEATHER.DAT (1st hour only)

Variables:

(DAY HOUR MIN UHM TSURF TAIR T6CM T15CM T30CM SW RSW VDA CLDOOV RAIN)

Example Data:

180	20	0	.69	300.14	300.08	302.32	300.10	297.33	106.62	20.86	.01806	.00
180	20	5	.61	299.79	299.88	301.99	300.10	297.35	94.39	18.32	.01831	.00
180	20	10	.56	299.35	299.75	301.76	300.10	297.38	82.28	15.87	.01861	.00
180	20	15	.50	298.96	299.61	301.48	300.10	297.40	70.45	13.56	.01870	.00
180	20	20	.44	298.48	299.48	301.19	300.10	297.43	58.92	11.39	.01878	.00
180	20	25	.50	298.06	299.29	300.94	300.13	297.45	48.00	9.34	.01908	.00
180	20	30	.52	297.67	299.05	300.60	300.13	297.48	38.08	7.37	.01937	.00
180	20	35	.61	297.32	298.95	300.26	300.13	297.50	29.43	5.64	.01956	.00
180	20	40	.65	297.05	298.78	299.95	300.13	297.53	22.49	4.24	.01955	.00
180	20	45	.60	296.71	298.53	299.67	300.13	297.55	16.84	3.10	.01941	.00
180	20	50	.61	296.42	298.23	299.34	300.10	297.55	12.36	2.30	.01923	.00
180	20	55	.55	296.08	297.82	299.07	300.08	297.55	8.72	1.67	.01916	.00

Table 10. Input data file for modeling and sensitivity parameters, FILE: PARAM.DAT

Parameters:

(M ITER DT FH FN FU FW FO TDEPTH ATOLER BTOLER CTOLER HTOLER)

Example Data:

15	15	300	0.6	0.6	0.6	0.6	.85	.15	5.0D-16	5.0D-14	5.0D-12	5.0D-18
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Parameters:

(IPH TCA OCARB APRATE SRESP NK1 NK2 FC02 FNI3 FSIK FRAC SC02)

Example Data:

6.4	1800.	1.04	120.	2.8D-08	1.9D-03	.66	10.	10.	1.0	.005	1.42D-4
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Table 11. Input data file for soil bulk density, assumed initial soil water content and temperature and soil characteristics, FILE: HAYNIE.DAT

Constant and Variable Soil Properties:

Line 1: BD (bulk density, Mg/m^3 , for each depth increment)
 Line 2: W (beginning water content, kg/kg, for each depth increment)
 Line 3: T (beginning temperature, $^{\circ}K$, for each depth increment)

Example Data:

1.155 1.165 1.175 1.185 1.195 1.205 1.215 1.225 1.235 1.245 1.255 1.265 1.275 1.285 1.295
 .05 .065 .079 .092 .104 .115 .125 .134 .142 .149 .155 .16 .164 .167 .169
 300.1 300.7 301.2 301.6 301.9 302.1 302.3 302.1 301.9 301.6 301.3 301. 300.7 300.4 300.2

Soil Characteristics:

(B1 PAE PDRAIN SAND SILT CLAY AT BT HT XT A1 A2 A3 A4)

Example Data:

3.2 -1.4 -2.5 .65 .28 .07 .45 .80 .20 6.0 8.7237D-6 1.27026D-4 4.716029D-4 2.1332D-3

MODELING UREA TRANSPORT AND AMMONIA VOLATILIZATION
UNDER FIELD CONDITIONS

by

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AN ABSTRACT OF A MASTER'S THESIS

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ABSTRACT

Ammonia volatilization loss from surface application of urea to bare soil is significantly influenced by soil type, environmental factors and fertilizer management practices. A one-dimensional, finite-difference model was developed to simulate transport of urea in soil and to predict volatilization loss of ammonia following application of urea to the soil surface. Field conditions were simulated in the model by using meteorological data collected during a 15-day field study of NH_3 volatilization. The predicted ammonia volatilization loss of 16.3 % (of applied urea-N) compared favorably with a field-measured loss of 17 %. For a major time period of the simulation, the modeled soil surface temperature remained within $\pm 2^\circ \text{C}$ of the measured soil surface temperature and the modeled and measured surface soil water content remained in the 1-3 % (kg/kg basis) levels. The model predicted that urea was transported in significant amounts to a depth of 4 cm following a simulated irrigation of 0.5 cm, approximately 6 days after application of urea. Compared to a 4 % field-measured loss for the 6-day period following application of urea, the model predicted a relatively smaller loss of 3 %. During the 6-day period, only 14.3 % of the urea applied was predicted to have hydrolyzed. However, urea was rapidly hydrolyzed following the first and second irrigations, on days 9 and 13 following application of urea. Nearly 100% of the applied urea was predicted to have hydrolyzed in 15 days. The model predicted peak losses of ammonia for the 4-day period between the second and third irrigations of 0.5 cm each.

A sensitivity analysis of the model showed that the predicted loss was reduced to 7.3% for a one-time irrigation of 2.54 cm, 4 hours after urea application. The magnitude of ammonia loss was found to positively correlate with the surface soil pH. The modeled loss was found to be extremely sensitive to the solubility of ammonia and, to a lesser degree, to the solubility of carbon dioxide. Sensitivity analysis suggested that under the predominantly dry conditions of the simulation the effect of the soil hydrogen-ion buffering capacity on ammonia loss may be masked by other dominating factors such as surface soil water content and temperature.

The model developed for this research was programmed in Microsoft FORTRAN and was run on an IBM compatible Personal Computer equipped with 640 K RAM and a numeric coprocessor. Three data files, namely, a meteorological data file, a parameter file and a soil characteristics file were used to run the model. The use of data files allowed the model to be run under a variety of conditions. A 15-day simulation was completed in 18 to 24 hours.